1975

Studies With Silicon Heterocycles.

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STUDIES WITH SILICON HETEROCYCLES

A Dissertation

Submitted to the Graduate Faculty of the
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in partial fulfillment of the requirements
for the degree of

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in

The Department of Chemistry

by

Joanne Moreau Wolcott
B.S., Louisiana State University, 1970

August, 1975

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Joanne M. Wolcott
August, 1975

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ABSTRACT

Organosilicon heterocycles have played an important role in the development of organosilicon chemistry. Some of the areas aided by the study of organosilicon heterocycles include: studies relating to polymers, bonding at silicon, and mechanisms of reactions at silicon. In this work, organosilicon heterocycles are employed in the study of two separate areas of organosilicon chemistry; the study of silalactone chemistry and the study of the effect of ring strain on reactions at silicon.

In the study of silalactone chemistry, the preparation of 3- and 4- carboxybenzyldimethylsilane is reported, along with conversion of the acids under pyrolytic and hydrolytic conditions to dimeric or polymeric silalactones and to silanols and disiloxanes. In some cases rather complex equilibria involving the various products can be displaced to result in virtually exclusive formation of one product. Of particular interest is a novel macrocyclic lactone dimer in the meta series which can be obtained in good yield. A general method for the preparation of the silalactones is proposed, and the monomeric lactone from 2-carboxybenzyldimethylsilane is reported. Spectral properties of the products are reported and discussed.

In the study of the effect of ring strain on reactions at silicon, derivatives of 1,2-dimethylsilacyclopentane were prepared in order to investigate the role of ring strain in determining the stereochemical path of reactions. The silyl hydride, chloride, fluoride, bromide and p-anisyl derivatives of 1,2-dimethylsilacyclopentane were prepared and their reaction stereochemistry was compared to that observed for the unstrained acyclic systems and the highly strained silacyclobutane

system. Some of the nucleophilic displacement reactions studied occurred with inversion of configuration at Si as was previously observed with the acyclic systems. Formation of isomerized product was, however, also noted in some cases in contrast to the acyclic systems previously studied. Mechanisms are proposed to account for the observed stereochemistries of the reactions studied.

The silacyclopentane system was also used to study further the mechanism of isomerization at silicon, catalyzed by polar aprotic solvents. A detailed study of the epimerization of 1-chloro-1,2-dimethylsilacyclopentane by hexamethylphosphoric triamide (HMPT) in CCl_4 is reported. The proposed mechanism for isomerization involves two pathways that have a first and second order dependence on HMPT. The second order pathway involves formation of intermediates similar to the ones proposed for the acyclic and silacyclobutane isomerizations. The proposed mechanism for the first order pathway involves formation of a trigonal bipyramidal intermediate that undergoes pseudorotations to give isomerization of the chlorosilane. The first order dependence on HMPT and the formation of isomerized product in the nucleophilic displacement reactions indicate that pseudorotations occur more readily in the silacyclopentane system than in the systems previously studied.

SECTION 1

The Preparation and Reactions of Silalactones

Chapter 1

The study of organosilicon chemistry began in 1863 when Friedel and Crafts prepared tetraethylsilane from diethylzinc and silicon tetrachloride. A great impetus was provided at the turn of the century when Kipping and others applied the newly discovered Grignard reagent to the synthesis of organosilicon compounds. World War II again stimulated tremendous growth in organosilicon chemistry due to interest in the wide applications of silicon polymers.[1] Although siloxane polymers are still commercially important today, the interests of basic research are now more concerned with carbon-functional organosilicon compounds and the elucidation of mechanisms of reaction at silicon.

Early interest in the field of organosilicon chemistry centered on the similarities between silicon and carbon as suggested by their relative positions in the periodic table. Carbon and silicon, indeed, share many periodic properties as exemplified by the ability of both elements to form catenates and tetracoordinate species. However, early researchers were surprised to learn that most organosilicon compounds differ significantly from their carbon analogs. In many cases, the differences in these systems are far more important than their similarities. In recent years, the emphasis has shifted to a study of the properties that differentiate these systems.

Several factors tend to distinguish an organosilicon compound from its carbon analog. These features include differences in atomic radii, ionization energies, electronegativities, π bonding, etc. Although all of these factors merit study, the presence of the silicon d-orbitals has been most often invoked to explain the differences observed.

In contrast to carbon, silicon can utilize its 3d orbitals to form pentacoordinate and hexacoordinate species. Several examples of extracoordinate silicon species have long been known. One of the first studied extensively was the hexafluorosilicate anion (Figure 1-1).[2]

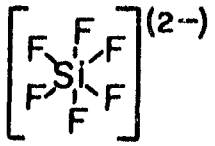


Figure 1-1

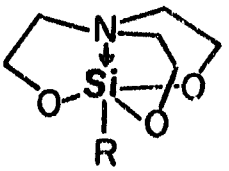


Figure 1-2

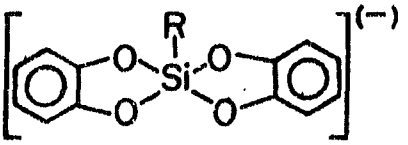


Figure 1-3

X-ray diffraction studies of its salts have revealed its octahedral geometry. Pentacoordinate species are also known such as the triptych-siloxazolidines (Figure 1-2)[3] and the anions of bis(o-phenylenedioxy) organosiliconic acid (Figure 1-3).[4] Although all of the extracoordinate species that are known contain several electronegative substituents, extracoordinate species with more alkyl substituents have been postulated as intermediates in several reaction schemes.[5,6]

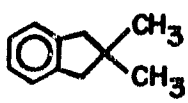
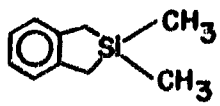
Silicon can also utilize its 3d orbitals to form p-d and d-d π bonds. Interactions of the d-d π type are proposed to be important in Si-Si bonded systems and the esr spectrum of the radical anion of dodecamethylcyclohexasilane[7] and the UV spectra of a series of permethyl-polysilanes[8] have been cited as evidence.

Much interest has been recently expressed in the ability of Si to form p-d π bonds. Although there is ample evidence that Si is an electron acceptor from attached π systems,[9] there is considerable controversy as to the importance of p-d π interactions.

A silicon atom can also interact with a functional group in the β position. Charge transfer spectra of XC_6H_5-TCNE complexes have been cited as evidence for a mesomeric rather than inductive effect in these

β interactions. H. Bock and others[10] have shown that the charge transfer band for a Si β to a phenyl ring is lower in energy than that of the carbon analog.(Table 1-1). Also the values for $(CH_3)_3Si-C_6H_5$ and $(CH_3)_3SiCH_2-C_6H_5$ (Table 1-1) should be reversed if an inductive effect is operative. More evidence for a mesomeric effect was advanced by Pitt and coworkers[11] who found that the lowering of the charge transfer band energy is reduced when Si is constrained in a ring.

TABLE 1-1

Compound	X-C_6H_5-TCNE Charge Transfer Band (cm^{-1})
$(CH_3)_3C-C_6H_5$	22,650[a]
$(CH_3)_3Si-C_6H_5$	23,600[a]
$(CH_3)_3SiCH_2-C_6H_5$	20,200[a]
	21,000[b]
	20,700[b]

[a] Reference 9

[b] Reference 10

Attempts to show β-interactions using the correlations of $^{29}Si-H$ and $^{13}C-H$ coupling constants with Hammett σ constants for a series of substituted toluenes have met with little success.[11] Trends indicate, however, that strongly electron withdrawing substituents on benzene might lead to more significant results.

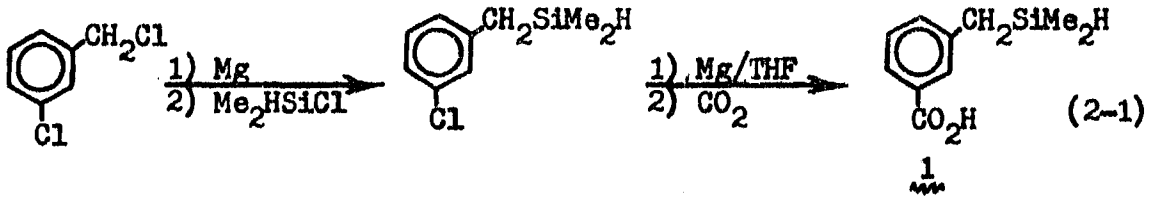
In this study, 3-carboxybenzyldimethylsilane was chosen to investigate the interactions between an aromatic ring and a silicon atom β to the ring, since a 1,3 interaction involving a Si d-orbital

would give hindered rotation about the ring-to-benzyl carbon bond.

Two types of interactions are possible in the 3-carboxybenzyldimethylsilane system: 1) a 1-3 p-d bonding in which electron density is donated from the phenyl ring to an empty d-orbital on Si[13], and 2) a hyperconjugative interaction involving a C-Si σ bond[14,15]. Either type of interaction could give rise to hindered rotation about the ring-to-benzyl carbon bond. This restriction to rotation of the side chain could in principle be observed by variable-temperature NMR, since the methylene protons or the methyl groups on silicon would become diastereotopic and potentially distinguishable when an ortho or meta substituent is present. The carboxy group seemed suitable because of the relatively large effects of carbonyl groups on chemical shifts of nearby protons. The meta isomer was chosen so that there would be no steric interactions between the carboxy and silylmethyl groups.

Chapter 2

The preparation of (3-carboxybenzyl)dimethylsilane, 1, was not as easy as had been anticipated. All attempts to prepare 1 by using standard Grignard preparations (Equation 2-1) were unsuccessful. Although there is ample precedent for the generation of a C-Mg bond in



(2-1)

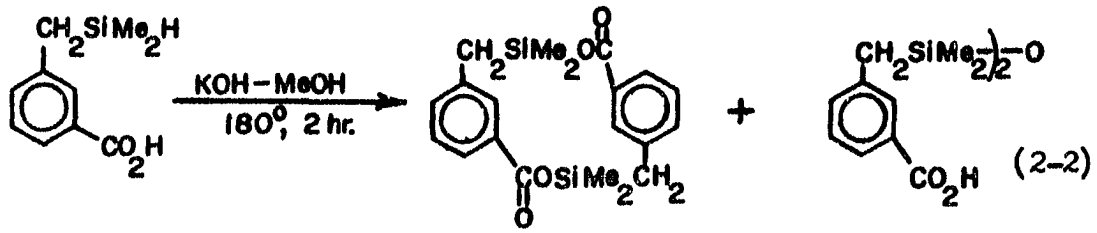
1

the presence of a Si-H bond,[16-18] it is usually necessary to use forcing conditions to generate Grignards from aryl chlorides. Indeed, the only method that resulted in the formation of the Grignard reagent from m-chlorobenzyldimethylsilane involved the use of powdered Mg,[19] prior activation of the Mg with dibromoethane, high chloride concentrations and prolonged heating of the reaction mixture. No reaction occurred when Mg turnings were substituted for powdered Mg. This procedure gave a fairly high yield of acid, 1, (80-90%) in the crude reaction mixture, indicating no apparent difficulties from involvement of the Si-H bond. However, decomposition of 1 during the vacuum distillation resulted in a lower yield of the pure compound.

During the distillation of 1 the first time it was prepared, relatively high pot temperatures (> 200°C) were reached and partial solidification of the pot mixture occurred. On further investigation into the nature of the solid, which showed spectroscopically the absence of a Si-H linkage, we were able to determine that heating acid 1 with base results in formation of a novel silalactone dimer, 2,* *4,4,13,13-tetramethyl-3,12-dioxa-4,13-disilatricyclo[13.3.1.1^{6,10}] eicosa-1(19),6,8,10(20),15,17- hexaene-2,11-dione.

Several silalactones with silyl ester linkages and one example of a dimer have been reported in the literature.[20-23] However, none have been prepared in this manner. Disilalactone, 2, is unique in several respects. It is the largest dimer reported in the literature, it reacts differently than previously reported silalactones, and it is the only silalactone that contains phenyl groups in the heterocyclic ring. Due to the novelty of this system, we decided that it merited further study.

In the absence of base, the conversion of acid, 1, to disilalactone, 2, proceeded very slowly at 180°. Under these conditions, approximately 10% of 1 had been converted to 2 after heating for 4 hr. Upon addition of methanolic KOH, complete conversion of the acid was achieved after heating at 180° for 2 hr.



(2-2)

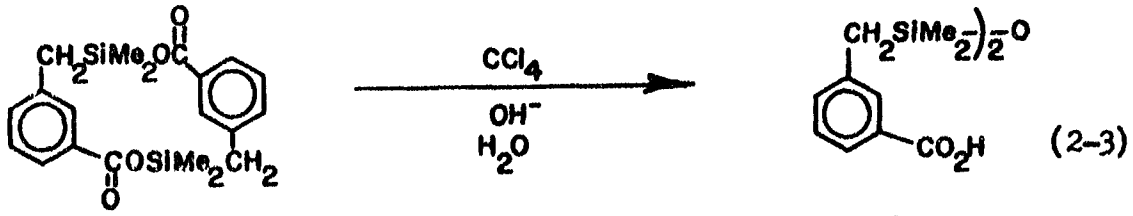
1 2 3

The product mixture contained 78% of 2 and 22% of (3-carboxybenzyl)dimethyldisiloxane, 3. The silalactone dimer could be readily purified by subliming it directly from the latter reaction mixture at 170° (0.5 mm). A white crystalline solid was obtained which became a viscous oil when exposed to atmospheric moisture.

The structure of 2 was elucidated using a combination of analytical techniques. The parent peak was observed at 385 m/e in the mass spectrum and an infrared spectrum gave the carbonyl stretch at 1700 cm^{-1} and the Si-O bands at 1080 and 1110 cm^{-1}. Disappearance of the Si-H signal in the IR and NMR was the major clue, however the NMR spectrum had other

notable features (see Figure 2-1). As is well known, aromatic protons ortho to a carbonyl function are shifted downfield. Dimer 2, however, showed a resonance even further downfield in the aromatic region (δ 8.4) which we assigned to the aromatic proton contained in the heterocyclic ring. Models indicated that this proton could come quite near the aromatic nucleus across the ring, thus being further deshielded. The chemical shift of the Si-Me protons was also interesting. At δ 0.4 they are substantially further downfield than the Si-Me protons of disiloxane 3 (δ 0.1) or silanol 4 (δ 0.2), which also have Si attached to oxygen.

When the reaction mixture from Equation 2-2 was dissolved in hot CCl_4 and exposed to moisture, 3, the disiloxane, crystallized out of the solution (Equation 2-3).



2 3 (2-3)

This reaction was not surprising since disiloxanes have been observed to form from silalactones upon the addition of moisture.[20,22] Mironov, et al., also observed that a disiloxane was converted to a silalactone on heating. Indeed, heating compound 3 at 190° for 1 hr. gave 20% of the disilalactone with 80% of 3 unconverted. Further heating caused no appreciable change in the composition of the product mixture. Since other workers reported that silalactones could be converted to disiloxanes by moisture alone, the sublimed disilalactone was dissolved in hot CCl_4 and exposed to moisture in the absence of any base. Instead of the

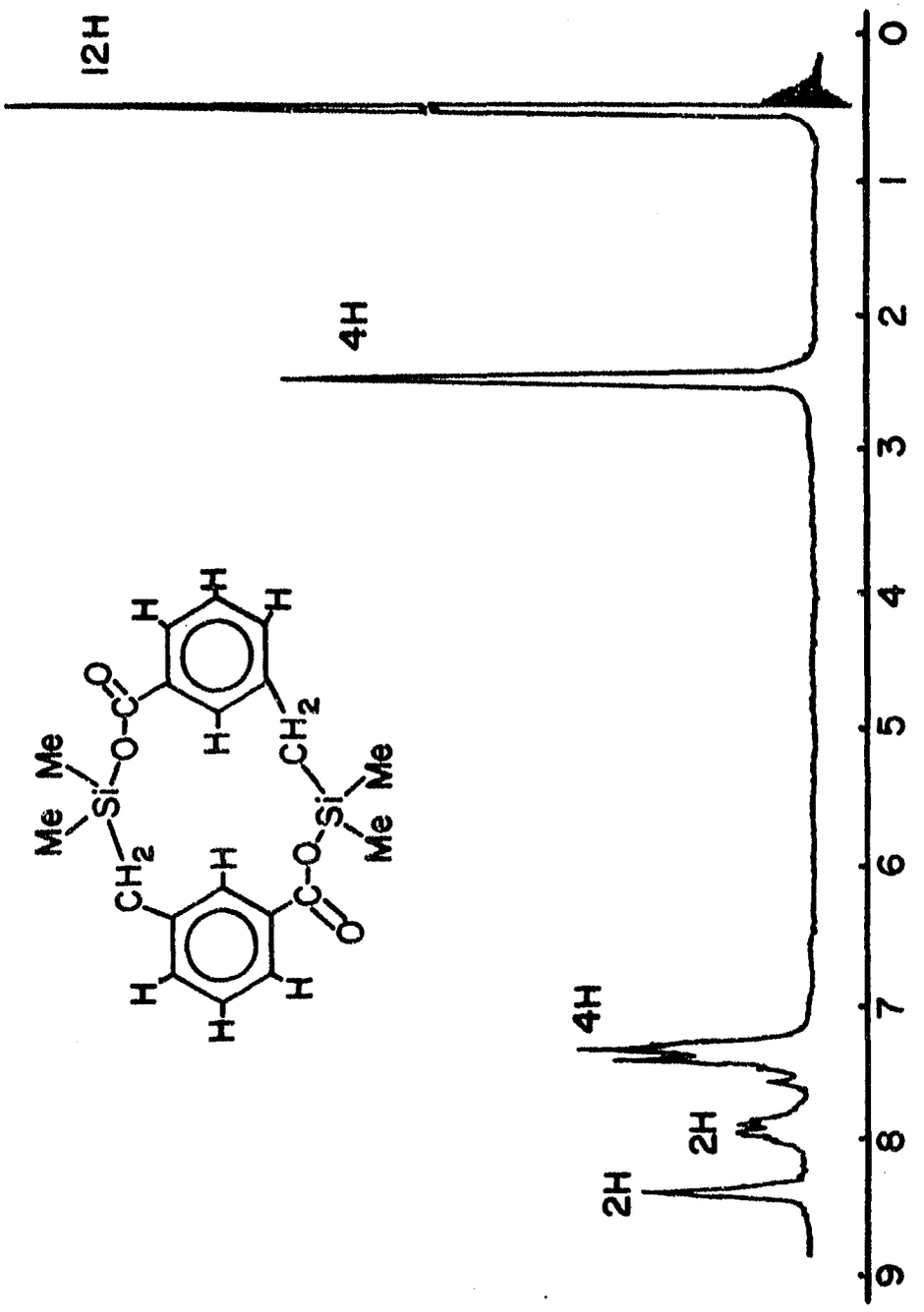
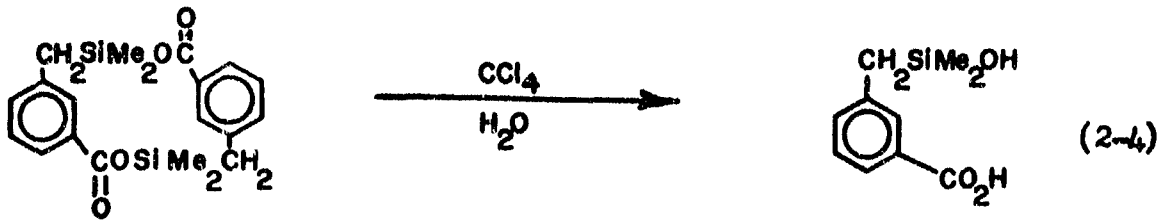


Figure 2-1. NMR Spectrum of Disilalactone 2.

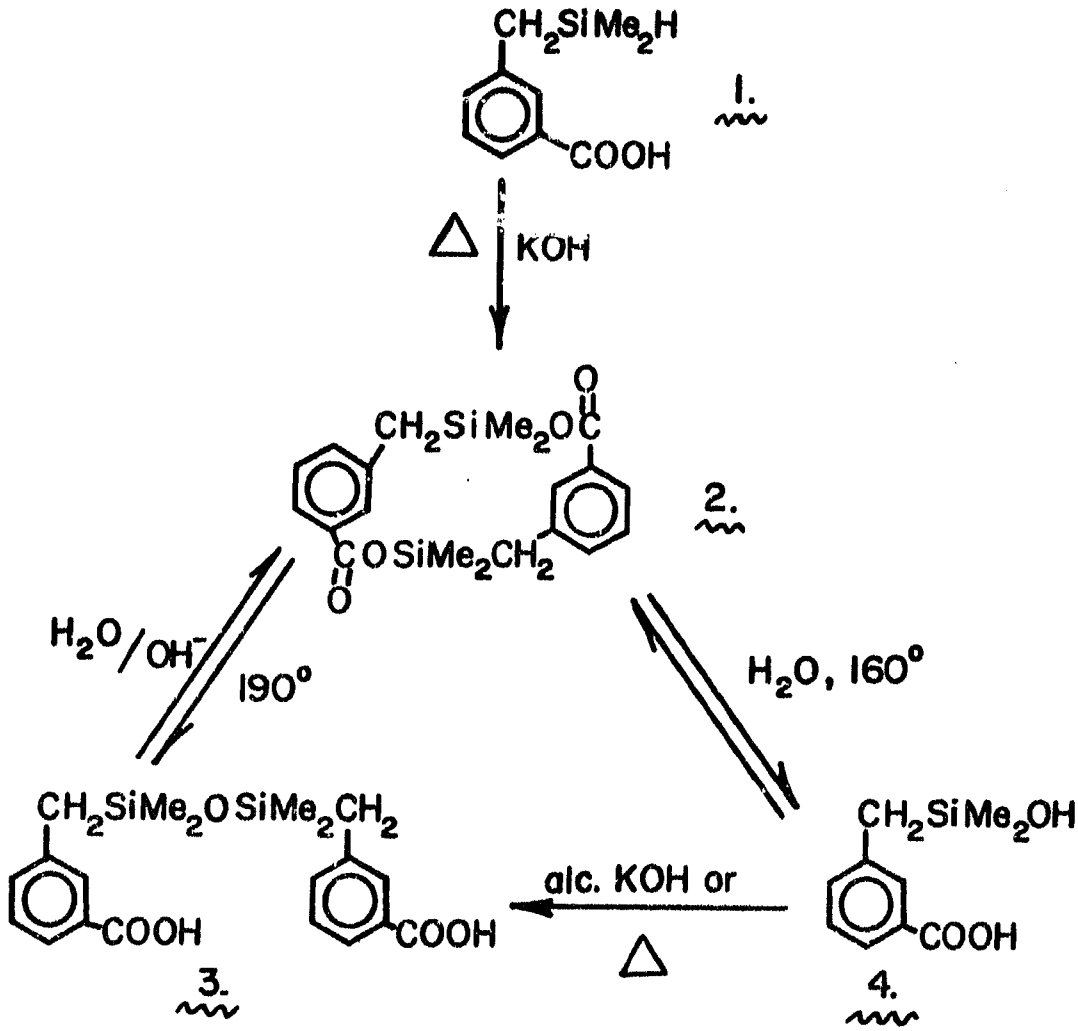
expected disiloxane, (3-carboxybenzyl)dimethylsilanol, 4, was obtained (Equation 2-4). The formation of a silanol from a silalactone has not



2 4 (2-4)

previously been reported, and we are somewhat surprised at the reluctance of 4 to yield disiloxane in protic media. Silanol, 4, did react in the usual manner with base to give disiloxane, 3. However, heating the silanol in the absence of base gives disilalactone, 2, and disiloxane, 3, in approximately equal quantities. The interconversions involving all of the species mentioned so far are summarized in Scheme 2-5. The system is, so far as we are aware, unique in allowing the formation of all of these related compounds under conditions where any one can be obtained as the almost exclusive product by appropriate minor adjustment of the reaction conditions.

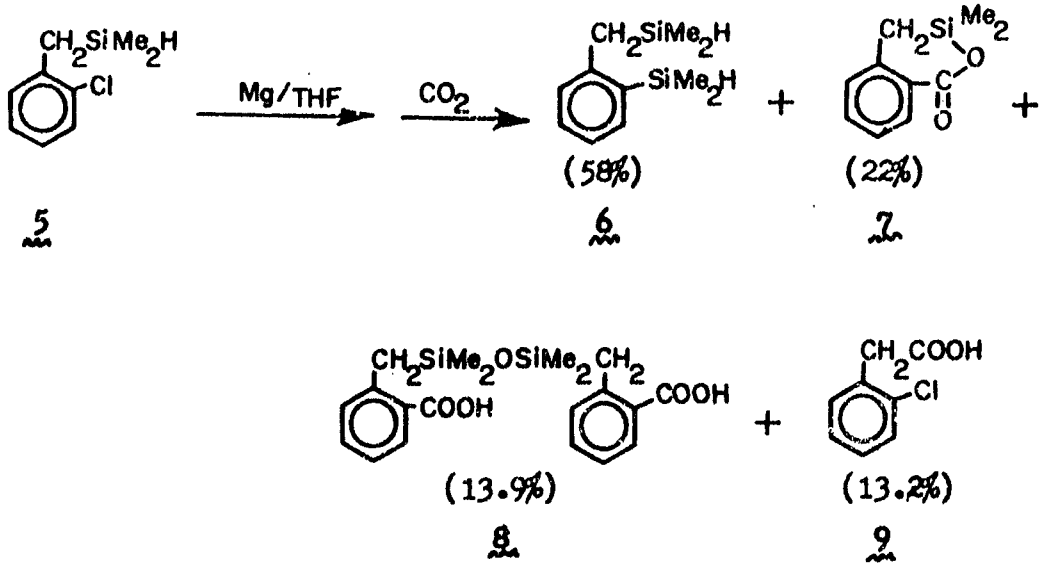
Determination of the temperature dependence of the NMR spectrum of hydrosilyl acid, 1, was one of the goals of this research. However, at temperatures as low as -80°C in acetone-d_6, no splitting of either benzylic or Si-Me signals could be observed. This observation is, of course, no direct proof against the existence of a hyperconjugative or other interaction. Evidence of an interaction in this system simply could not be seen by using this technique due to peak broadening caused by freezing of the sample. An interaction could possibly be seen if a more dilute sample could be used and lower temperatures could be reached.



Scheme 2-5

The literature with respect to preparation of ω-silalactones is very sparse and the preceeding work gives promise of affording a general method for their preparation from readily available starting materials. The generation of silanol and carboxylic acid functions together should give formation of silalactone if the ring size is appropriate. In order to test the generality of this synthesis and because of the continuing interest in the spectroscopic properties of the hydrosilyl acids, the work was extended to the corresponding ortho and para derivatives.

o-carboxybenzyldimethylsilane could be expected to be a precursor for a six-membered ring silalactone or conceivably a twelve-membered dimer which could be compared with 2. The Grignard reagent of (2-chlorobenzyl)dimethylsilane, 5, was prepared using the method developed for compound 1. The usual carbonation and workup with mild acid hydrolysis gave a crude reaction mixture which apparently, from its NMR spectrum, contained none of the expected o-hydrosilyl acid. Careful fractional distillation afforded the components of the mixture shown in Scheme 2-6.



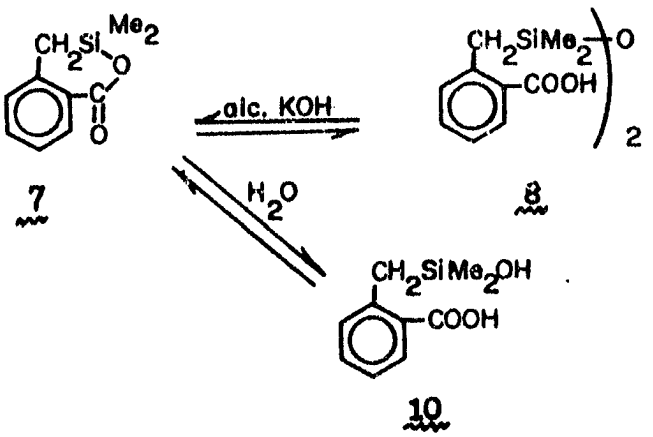
5 6 7 8 9

(2-6)

The silalactone, 7, was obtained (in impure form) on distillation of

the reaction mixture which had been subjected to hydrolysis in the presence of mild acid. Such conditions are normally not sufficient to result in Si-H hydrolysis, so we presume that lactone was formed immediately on carbonation, with carboxylate anion displacing hydride. Simple propinquity plus the resonable stability of the silalactone apparently afford sufficient driving force to make the displacement proceed.

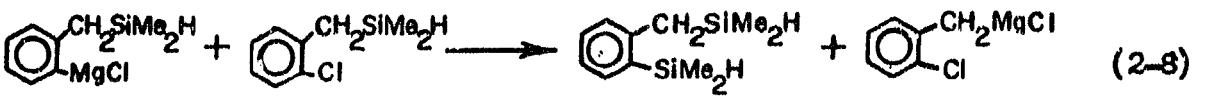
Pure disiloxane, 8, was obtained only after distilation fractions were extracted with mild base. The yield quoted was derived from NMR spectra of the first distilation products. It is possible that some 8 may have been formed on hydrolysis of 7. Indeed, in a separate experiment, silalactone, 7, in CCl_4 was treated with alcoholic KOH to reach an equilibrium mixture of 7 and 8 in a 5:3 ratio, respectively. Exposing compound 7 to moisture gave an equilibrium mixture of 7 and a compound that could not be isolated in pure form but was tentatively identified as (2-carboxybenzyl)dimenthylsilanol, 10(Scheme 2-7). The reactions of 7 were consistent with those observed for the silalactone dimer, 2; however, in contrast to the behavior of 2, 7 reacted more slowly and formed equilibrium



(2-7)

mixtures that contained appreciable quantities of itself. The greater stability of 7 is probably due to the favorable six-membered ring geometry, while the macrocycle, 2, is more like a normal silyl ester.

The main product in Scheme 2-6 was a considerable surprise. The disilyl derivative, 6, was easily isolated by distillation and identified as the same compound previously prepared[24] by a standard procedure. The disilyl compound was apparently formed when one molecule of Grignard attacked the Si atom of another molecule of starting material, displacing the benzyl anion (Equation 2-8). Cleavage of a benzyl group from Si by

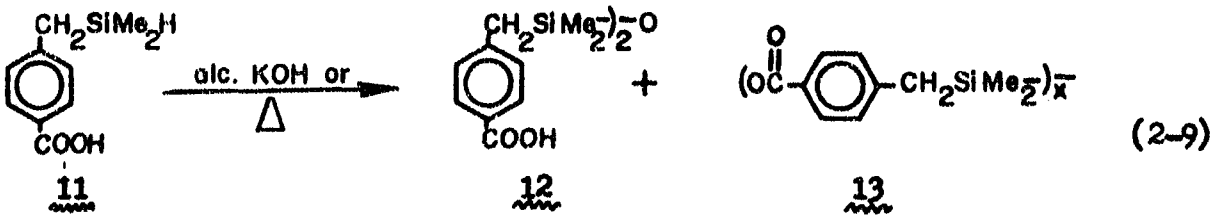


(2-8)

a Grignard reagent has in fact been previously observed.[25] In agreement with reaction (2-8), o-chlorophenylacetic acid, the carbonation product from the benzyl fragment, was also isolated. The observation of benzyl anion displacement with the ortho Grignard reagent, but not with the meta reagent, might be attributed to some kind of electronic effect. However, this seems unlikely, particularly since it is also not observed with the para reagent (vide infra). Perhaps Grignard and starting chloride complex with one another but only in the case of the ortho derivative is there a reasonable steric disposition for nucleophilic attack on Si.

The Grignard reagent of p-chlorobenzyldimethylsilane was prepared and carbonated to obtain a good yield of the expected para hydrosilyl acid, 11. This acid could not be anticipated to be the precursor for a monomeric silalactone, and models of the lactone dimer seem significantly strained. When the acid was heated in the presence of alcoholic KOH, a complex product mixture was formed. However, the most prominent Si-Me peak in the NMR spectrum of the mixture was a singlet at δ 0.4 ppm which we tentatively ascribed to a polymeric silyl ester. Also in agreement with this assignment is the observation that the peak eventually disappears on exposure to moisture. When the acid is heated without base,

only two main products are formed, which we tentatively identify as polymer and disiloxane (Equation 2-9).



11 12 13 (2-9)

The NMR spectra of the compounds described were quite simple, a fact that made it possible to follow spectrally some of the complex hydrolysis equilibria encountered. Silanol, 10, disiloxane, 12, and polymer, 13, were tentatively identified from their NMR spectra. The mass spectra of silanol, 10, and disiloxane, 8, were essentially identical with that of lactone, 7, indicating quite facile dehydration, perhaps occurring thermally, prior to ionization. Disiloxane, 12, also showed the fragment at m/e 192, $O_2CC_6H_4CH_2SiMe_2$, and this peak grew as inlet temperature was raised, again indicating the possibility of pyrolysis.

The silalactone synthesis reported in the preceeding study seems to be general for the type of system studied assuming that the silalactone formed will distill or sublime from the reaction mixture. Further study is needed, however, before the synthesis can be extended to aliphatic systems. The reactions of the silalactones studied were similar in many ways to those reported in the literature; however, differences were noted. The silalactones reacted with moisture to give silanols rather than the previously reported disiloxanes. This difference was probably due to the presence of the aromatic ring since the other systems studied were aliphatic in nature.

Experimental Section

General for all Chapters

Unless otherwise stated, all Grignard and lithium reagents were prepared in three-neck round-bottom flasks equipped with a reflux condenser, a magnetic stirrer, and an addition funnel. The glassware was oven dried, assembled hot, and flushed with nitrogen prior to conducting the reaction under a nitrogen atmosphere. Tetrahydrofuran (THF) was dried by distilling from calcium hydride and then shaking with Linde 5A molecular sieves. Hexamethylphosphoric triamide (HMPT) and dimethylformamide (DMF) were dried by distilling from calcium hydride. Carbon tetrachloride and chloroform were dried by shaking with Linde 4A molecular sieves. The low temperature NMR study and spectra of some of the major products were run on the Varian HA-100 NMR Spectrometer. Routine NMR spectra were recorded using a Varian A60A spectrometer and unless otherwise specified the chemical shifts reported are relative to internal TMS. In some cases benzene or CH_2Cl_2 were used as internal standards instead of TMS. The standard if different from TMS is noted in parentheses after the solvent. A Varian V-4343 Variable Temperature Controller was used to control the sample temperature.

Infrared spectra were obtained using a Perkin-Elmer 137 Infracord spectrophotometer. Mass Spectra were recorded on a Hitachi-Perkin-Elmer RMS-4 Mass Spectrometer operating at 70 eV ionization potential and data are reported as m/e (relative intensity). A Perkin-Elmer Model 900 Gas Chromatograph equipped with a flame ionization detector was used for routine gas-liquid partition chromatography (glpc). GLPC- Mass Spectra were obtained on a Perkin-Elmer 990 Gas Chromatograph interfaced through a Biemann-Watson separator to a Hitachi-Perkin-Elmer RMS-4 Mass Spectro-

meter. The spinning band distillations were done on a Nester-Faust Auto Annular Still.

Preparation of (3-carboxybenzyl)dimethylsilane(1).

Magnesium powder (0.16 mole, 3.9 g) and 50 ml of dry THF were placed in a round-bottom flask. The magnesium was activated by the addition of 1 ml dibromoethane and refluxing for 15 min. (3-Chlorobenzyl) dimethylsilane (0.11 mole, 20.4 g) was added dropwise while refluxing the reaction mixture. An additional 25 ml of dry THF was added to the reaction vessel about 4 hr. later. After refluxing for 24 hr., the Grignard reagent was poured into a slurry of dry ice in 50 ml THF, and stirred with a mechanical stirrer until the dry ice had sublimed. The organic layer was then hydrolyzed with dilute HCl, separated, and washed with H_2O. The solvent was removed using a rotary evaporator. Dry ether (25 ml) was added to the remaining material and this solution was dried over anhydrous $MgSO_4$ for several hours. The solvent was removed and the remaining material was vacuum distilled to yield 9.55 g (31%) of 1, bp 109-110° (0.3 mm). NMR (CCl_4): δ 0.05 (d, J=4Hz, 6H), 2.15 (d, J= 3Hz, 2H), 3.9 (broadened septet, 1H), 7.2-7.8 (m, 4H), 11.7 (s,1H). IR (neat): 3000, 2600, 2100, 1675, 1600, 1400, 1260, 1240, 1200, 1150, 1060, 900, 850, 820, 780, 760, 750, and 680 cm^{-1}. Anal. calcd. for $C_{10}H_{14}SiO_2$: C, 61.81; H, 7.26; Found: C, 61.81; H, 7.38.

Preparation of silalactone dimer(2).

(3-Carboxybenzyl)dimethylsilane (0.0078 mole, 1.52 g) and 0.6 ml of 0.46M KOH in anhydrous methanol were placed in a round-bottom flask and heated at 170° for 2 hours under a nitrogen atmosphere. An NMR spectrum indicated that approximately 78% of the acid had been converted to the disilalactone. The disilalactone was then sublimed from the

product mixture at 170° (0.5 mm) to yield 1.00 g (67%) of 2, mp 152-155°. NMR ($CDCl_3$): δ 0.4 (s, 6H), 2.4 (s, 2H), 7.2-7.5 (m, 1H), 7.7-8.0 (s, 1H), 8.4 (s, 1H). IR (Nujol): 1600, 1280, 1240, 1210, 1110, 1060, 930, 920, 840, 815, 790, 775, 755, and 690 cm^{-1}. Analysis calculated for $C_{20}H_{24}Si_2O_4$: C, 62.46; H, 6.29. Found: C, 62.30; H, 6.37. Mass Spectrum: 384(30), 192(18), 179(13), 165(14), 149(18), 119(16), 118(70), 90(100), and 89(25).

Preparation of (3-carboxybenzyl)dimethylsilanol(4)

The purified silalactone dimer obtained in the previous procedure was dissolved in hot CCl_4 and left open to atmospheric moisture. After 2 days, the silanol, a white fluffy solid, precipitated from the solution. An NMR spectrum showed that greater than 95% of the disilactone had been converted to the silanol. The silanol was recrystallized from hot $CHCl_3$ to give 0.6 g (50%) of 4, mp 115-117°. NMR ($CDCl_3$): δ 0.2 (s,6H), 2.3 (s, 2H), 6.8 (s, 2H), 7.2-7.4 (m, 2H), 7.7-7.9 (m, 2H). IR (Nujol): 3300, 2800, 2700, 1650, 1600, 1350, 1150, 1125, 1060, 1050, 900-750, and 680 cm^{-1}. Analysis calculated for $C_{10}H_{14}SiO_3$: C, 57.11, H, 6.71. Found; C, 56.96, H, 6.80.

Preparation of (3-carboxybenzyl)dimethyldisiloxane(3)

(3-Carboxybenzyl)dimethylsilane (1.27 g, 0.0067 mole) and 0.4 ml of 0.46M KOH in anhydrous methanol were placed in a round-bottom flask. The mixture was heated at 166° for 3 hr. The product mixture was then dissolved in hot CCl_4 and left open to moisture. After 2 days, the disiloxane, a white crystalline solid, precipitated from the solution. An NMR indicated that greater than 95% of the disilalactone had been converted to the disiloxane. After recrystallization from hot CCl_4, 0.70 g (54%) of pure disiloxane, mp 143-145°, were collected.

NMR ($CDCl_3$): δ 0.1 (s, 6H), 2.2 (s, 2H), 7.2-7.4 (m, 2H), 7.7-7.9 (m, 2H), 10.2 (s, 1H). IR (Nujol): 2800, 2600, 1650, 1575, 1400, 1260, 1240, 1200, 1150, 1060, 950, 900, 840-780, 750 and 685 cm^{-1}. Analysis calculated for $C_{20}H_{26}Si_2O_5$: C, 59.67; H, 6.51. Found: C, 59.22; H, 6.53.

Preparation of (2-chlorobenzyl)dimethylsilane(5)

Magnesium turnings (0.68 moles, 16.5 g) and 400 ml of dry ether were placed in a round-bottom flask. The magnesium was activated by the addition of 1 ml dibromoethane and stirring for 15 min. A mixture of 2-chlorobenzyl chloride (0.62 mole, 98.5 g) and 400 ml dry ether was added dropwise. After all of the mixture had been added, the solution was refluxed for 1 hr. The Grignard reagent was than added dropwise to a mixture of dimethylchlorosilane (0.62 mole, 60.2 g) and 200 ml dry ether. After the addition was completed, the solution was refluxed for 2 hr. The solution was then hydrolyzed with dilute HCl, separated, and washed with H_2O. The organic layer was dried over anhydrous $MgSO_4$, and then the ether was removed using a rotary evaporator. The remaining material was vacuum distilled to yield 67.6 g (59%) of 5, bp 59°(2 mm). NMR (CCl_4): δ 0.0, (d, J=4Hz, 6H), 2.25 (d, J=3Hz, 2H), 3.95 (broadened septet, 1H), 6.8-7.3 (m, 4H). IR (neat): 3000, 2130, 1470, 1440, 1250, 1220, 1160, 1050, 1030, 900, 840, 785, 770, 750, and 700 cm^{-1}. Analysis calculated for $C_9H_{13}SiCl$: C, 58.51; H, 7.09; Si, 15.20. Found: C, 58.27; H, 7.12; Si, 15.15.

Preparation of α,o-bis(dimethylsilyl)toluene(6)

The preparation was accomplished by using the procedure outlined in the preparation of (3-carboxybenzyl)dimethylsilane. The product was vacuum distilled to yield 7.46 g (65%) of 6, bp 57° (0.3 mm). NMR(CCl_4):

δ 0.0, (d, J=4Hz, 6H), 0.25, (d, J=4Hz, 6H), 2.25, (d, J=3Hz, 2H), 3.95, (broadened septet, 1H), 4.55, (septet, J=3Hz, 1H), 6.8-7.4, (m, 4H). IR (neat): 3000, 2150, 1600, 1460, 1450, 1260, 1200, 1150, 1120, 900, 840, 790, 750, 715, and 680 cm^{-1}. Analysis calculated for $C_{11}H_{20}Si_2$: C, 63.38; H, 9.67; Si, 26.95. Found: C, 63.43; H, 9.61; Si, 27.04.

The residue from the vacuum distillation was further distilled at 85-105° (0.3 mm) and three fractions were collected. The fraction collected at 85-95° was dissolved in ether and washed twice with 5% $NaHCO_3$. The ether layer was dried over anhydrous $MgSO_4$ and the ether was evaporated. The residue was vacuum distilled at 91° (0.3 mm) to yield pure lactone, 7. NMR ($CDCl_3$): δ 0.4, (s, 6H), 2.31, (s, 2H), 7.1-7.5, (m, 3H), 8.0-8.4, (m, 1H). Mass Spectrum: 192(25), 133(74), 118(67), 90(100), 89(68), 63(20). Analysis calculated for $C_{10}H_{12}SiO_2$: C, 62.45; H, 6.29. Found: C, 62.65; H, 6.14.

The fraction collected at 100-105° was dissolved in ether and washed twice with 5% $NaHCO_3$ solution. The aqueous layer was acidified and washed with ether. The ether was removed and the residue was recrystallized from an ethanol-H_2O solution and a white powder precipitated that was identified as disiloxane, 8, mp 87-89°. NMR ($CDCl_3$): δ 0.0, (s, 6H), 2.8, (s, 2H), 7.0-8.2, (m, 4H), 9.5, (s,1H). Analysis calculated for $C_{20}H_{26}Si_2O_5$: C, 59.67; H, 6.51. Found: C, 59.92; H, 6.75.

The filtrate from the previous crystallization was washed with ether. The ether solution was concentrated and petroleum ether was added until the solution became cloudy. A white crystalline precipitate was collected and identified as (o-chlorophenyl)acetic acid, 9, mp 94-96°.

NMR ($CDCl_3$): δ 3.85, (s, 2H), 7.2-7.5, (m, 4H), 11.4, (s, 1H). Mass Spectrum: 172(18), 170(51), 135(69), 127(35), 125(100), 91(61), 90(22), 89(31).

Preparation of (4-carboxybenzyl)dimethylsilane(11)

The preparation was accomplished using the procedure outlined in the preparation of 1. The product was obtained by dissolving the reaction mixture in diethyl ether, adding petroleum ether until the solution became cloudy. The product precipitated as a white, fluffy solid to yield 16.49 g (78%), mp 121-124°. NMR ($CDCl_3$): δ 0.05,(d, J=4Hz, 6H), 2.3, (d, J=3Hz, 2H), 3.9, (broadened septet, 1H), 7.1-7.4, (m, 2H), 7.9-8.2, (m, 2H), 12.1, (s, 1H). IR (Nujol): 3000, 2100, 1700, 1630, 1430, 1310, 1290, 1250, 1220, 1190, 1080, 950, 900, 870, 840, and 750 cm^{-1}. Analysis calculated for $C_{10}H_{14}SiO_2$: C, 61.61; H, 7.26. Found: C, 61.71; H, 7.12.

Preparation of (4-carboxybenzyl)dimethyldisiloxane(12)

(4-Carboxybenzyl)dimethylsilane (0.87 g, 0.0046 mole) and 0.4 ml of 0.46M KOH in anhydrous methanol were placed in a round-bottom flask. The mixture was heated at 150° for 1 hour. An NMR of the mixture indicated that about 50% of the acid had reacted. The reaction mixture was dissolved in ether and exposed to moisture for a few days. Petroleum ether was added to the ether solution until the solution became cloudy. A powdery precipitate was collected. The filtrate was concentrated and the disiloxane precipitated from solution yielding 0.1 g (10%) of pure product, mp 108-110°, after several recrystallizations. NMR (d_6-acetone) δ 0.0, (s, 6H), 2.0, (s, 2H), 6.1, (s, 1H), 7.0-7.2, (m, 2H), 7.7-8.0, (m, 2H). Analysis calculated for $C_{20}H_{26}Si_2O_5$: C, 59.67; H, 6.51. Found: C, 59.63; H, 6.72.

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SECTION 2

The Reactions and Isomerizations of the 1,2-Dimethylsilacyclopentane Ring System

Chapter 1

Until fairly recently there was a complete lack of information concerning the stereochemistry of substitution reactions at asymmetric silicon atoms. The lack of research in this area was due to the difficulties involved in the preparation and isolation of asymmetric silicon species. Unlike carbon, optically active organosilicon species are not found in nature and, thus, are not directly available from natural sources. In the early 1900's, F.S. Kipping succeeded in making optically active organosilicon compounds[1]. These compounds were, however, tedious to prepare and the optical rotations were so feeble that stereochemical studies were impossible.

The first optically active organosilicon compound with active functional substituents was prepared by Sommer and Frye[2] in 1958. Subsequent studies of their α-napthylphenylmethylsilanes demonstrated that reactions at Si are highly stereospecific. Since this original work proved so promising, stereochemical studies have become increasingly important in mechanistic investigations of organosilicon reactions.

Sommer originally defined two classes of mechanisms for nucleophilic displacement at Si which were the S_N2-Si and S_Ni-Si mechanisms.[3] The S_N2-Si mechanism (Figure 1-1) is similar to the S_N2 mechanism at

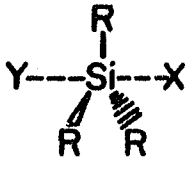


Figure 1-1. S_N2-Si Transition State

carbon. The entering and leaving groups occupy the axial positions in a trigonal bipyramid and the reaction proceeds with inversion of configuration. However, in contrast to carbon chemistry, it is possible to

have five full bonds to Si in the intermediate. Stable pentacoordinate Si species are known, and five coordinate intermediates have been demonstrated in several studies[4,5].

In the S_Ni-Si mechanism, the entering group provides electrophilic assistance in the rupture of the Si-X bond (Figure 1-2) and the reaction proceeds with retention of configuration at Si.

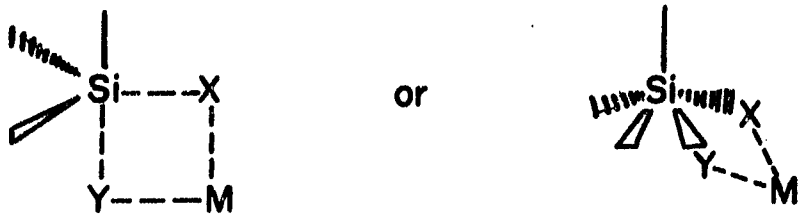
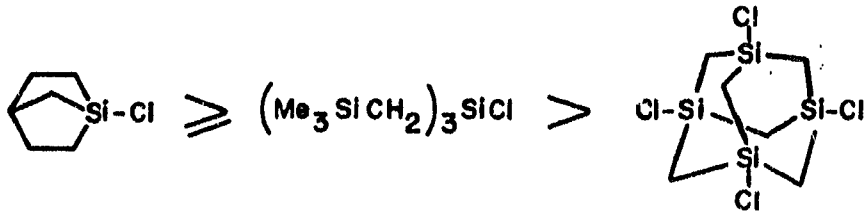


Figure 1-2. S_Ni-Si Transition State

Sommer originally proposed the "leaving group rule"[3,6] to explain the stereochemistry of nucleophilic substitution at silicon. A good leaving group would be displaced by the S_N2-Si mechanism and a poor leaving group would be displaced by the S_Ni-Si mechanism. Later studies showed that many factors are important in determining the stereochemistry of substitution. These factors include the nature of the organic groups on Si[7,8], the nature of the attacking group[9], and the nature of the solvent[4], in addition to the nature of the leaving group.

Silicon heterocycles have been useful in studying the effect of the organic groups attached to Si on the stereochemical path of reactions at Si. Several years ago, Sommer reported the preparation of 1-chloro-1-silabicyclo-[2.2.1]-heptane[10]. He found that this compound was highly reactive toward both hydrolysis and reduction by $LiAlH_4$, in contrast to the relative inertness of the analogous carbon compound. Later

comparisons of the bicycloheptane system showed the general trend in reactivity illustrated below[11]. The silicon atoms in both the tetra-



silaadamantane system and the bicycloheptane system are unable to undergo backside displacement due to the constraints imposed by the rings. The major difference in these systems lies in the degree of angle strain at Si.

The importance of angle strain at Si in determining the stereochemical path of a reaction has been recently demonstrated in other strained systems. Both retention and inversion are possible in the 1-phenyl-1-silaacenaphthene ring system investigated by Roark and Sommer[7], however, all of the substitution reactions observed went by retention of configuration at Si. The stereochemistry of several reactions in the 1,2-dimethylsilacyclobutane ring system have also been investigated, and all of them proceeded stereospecifically with retention[8,12].

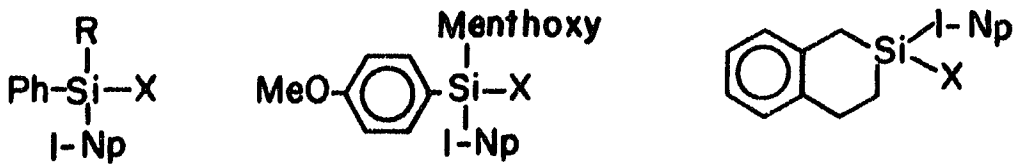
The observation of retention reactions at Si is not unique for systems with angle strain. As explained earlier, it often occurs with poor leaving groups. In angle strained systems, however, retention also occurs when there is a good leaving group.

The influence of angle strain on stereochemistry has been rationalized as being due to the fact that the angle strain would increase if the substituents on Si occupied their normal equatorial positions in the S_n2-Si transition state proposed for inversion mechanisms[8,11].

Similar effects of angle strain have been observed in phosphorus chemistry. In a recent summary of displacement mechanisms involving four-coordinate phosphorus, Koizumi and Haake[13] compared rates of substitution on strained cyclic phosphinates ($R_2XP{=}O$) with unstrained acyclic analogs. Ring strain may result in either acceleration or retardation of the rate of displacement. Rate acceleration was rationalized in terms of rapid formation of a pentacoordinate intermediate due to the availability of a 90° C-P-C bond angle. The intermediate would have a long enough lifetime for pseudorotations (in this case the exchange of axial and equatorial positons in a trigonal bipyramid) to occur. Retardation of the rate would occur in direct displacements involving backside attack due to the necessity of expanding the C-P-C bond angle. It is possible to argue that Si may also react through a similar mechanism, however, more data must be gathered before a firm conclusion can be reached.

The isomerization of asymmetrical Si species by various agents has often been proposed to involve the formation of extracoordinate species. Sommer first noticed the racemization of α-naphthylphenylmethylsilyl fluorides by methanol[14], and explained the results in terms of either a square-pyramidal intermediate with methanol at the apex that would racemize upon loss of methanol or formation and pseudorotation of a trigonal bipyramidal species.

Corriu later reported that racemization of the silyl chlorides and bromides[15,12] (shown below) by HMPT, is second order in HMPT.



He rationalized his data in terms of formation of a neutral hexacoordinate silicon species or a pentacoordinate siliconium ion (Figure 1-3).

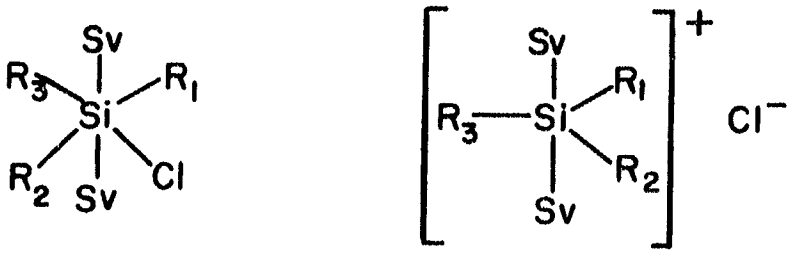


Figure 1-3

Either species would be symmetrical and it would not be necessary to invoke pseudorotation to account for the isomerization.

In this work, 1,2-dimethylsilacyclopentane derivatives were prepared in order to investigate more fully the role of ring strain in determining the stereochemistry of nucleophilic substitutions at Si and to elucidate further the mechanism of isomerization at Si. The silacyclopentane ring system is not significantly strained in comparison to the silacyclobutanes and silaacenaphthene ring systems; however, a direct displacement with axial entering and leaving groups would place considerable strain on the system. One of the early postulates of organophosphorus stereochemistry was that four- as well as five-membered rings could be expected to span an axial and an equatorial position in a trigonal bipyramid intermediate[18,19]. Retention is thus the normal stereochemistry for displacement and reduction reactions in four- and five-membered phosphorus rings. Nevertheless, there is a known example involving nucleophilic displacement on a phospholanium ion in which inversion is observed[19]. In this case, there is, presumably, an intermediate with the ring bonds equatorial.

The 1,2-dimethylsilacyclopentane system should be useful in determining the amount of strain that is required to produce certain effects.

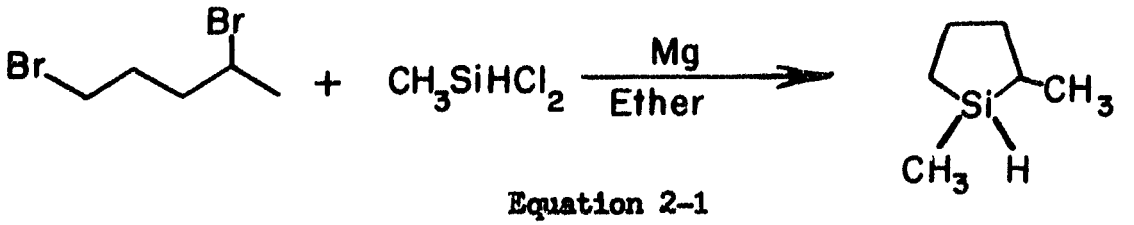
An intermediately strained ring of this nature, which will allow stereochemical studies, has not been previously prepared. Comparisons of the reactions of this system with those of strained systems like the ones previously mentioned[7,8] and with unstrained systems such as those of Corriu[20], Sommer[3], and Sakurai[21] should result in a clearer understanding of the effect of strain on the mechanism of reactions at Si.

The 1,2-dimethylsilacyclopentane system would also be useful in elucidating the mechanisms of solvent induced isomerizations at Si. Second order rate dependance on solvent would give more credence to Corriu's hexacoordinate intermediate since more angle strain would be involved in the siliconium ion intermediate. Whereas first order dependence on solvent would indicate either a square pyramidal transition state or a pseudorotation mechanism similar to those proposed by Sommer. Pseudorotation has been demonstrated for SiF_5^- and $R_2SiF_3^-$ systems by NMR[22] and it is possible that it may also be important in some mechanisms at Si.

Chapter 2

As previously mentioned, the 1,2-dimethylsilacyclopentane derivatives were chosen in order to study the effect of ring strain on the mechanisms of reactions at Si. This system seemed suitable since the relative positions of the methyl groups afforded the formation of geometrical isomers. It was hoped that these isomers would be readily separable without resorting to the elaborate techniques employed with optical isomers. Since changes in stereochemistry at Si would result in interconversion of geometrical isomers which differ in spectral properties, methods other than measurements of optical rotation could be used to follow the reactions at Si. This system would, therefore, be easier to study than the systems of optical isomers that were investigated by many other workers[3,7,20].

The compound, 1,2-dimethylsilacyclopentane (14) was prepared from the di-Grignard reagent of 1,4-dibromopentane and methyldichlorosilane (Equation 2-1). Comparable yields were obtained by mixing all of the reactants in one pot or by initial formation of the Grignard reagent followed by addition to the chlorosilane. The ring closure reaction



Equation 2-1

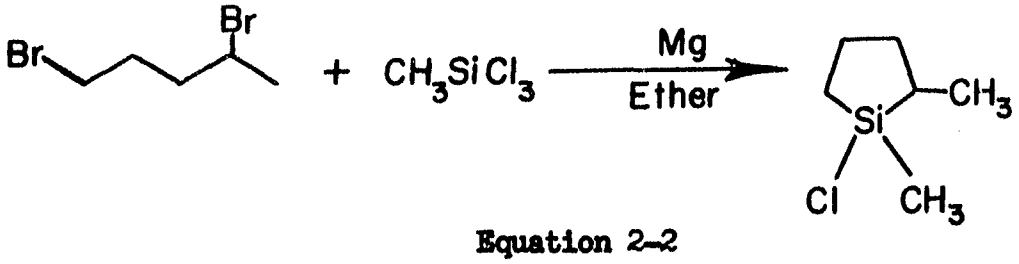
resulted in an approximately 50:50 mixture of the Z and E isomers; however, careful spinning band distillation resulted in fractions of greater than 98% isomeric purity. The structures of isomers 14a and 14b (Figure 2-1) were assigned from their proton chemical shifts in a manner analogous to that used for the silacyclobutane isomers[6]. Methyl

groups cis to one another are mutually shielding, while a methyl cis to

Figure 2-1. The proton chemical shifts were measured in CCl_4 with benzene as an internal standard[4] and are reported in ppm downfield from TMS.

the SiH proton shields that proton, thus the isomer with Si-Me and Si-H chemical shifts at δ0.055 and 4.01, respectively, was assigned the Z (cis) structure while the isomer with Si-Me and Si-H chemical shifts at δ 0.13 and 3.83, respectively, was assigned the E (trans) structure.

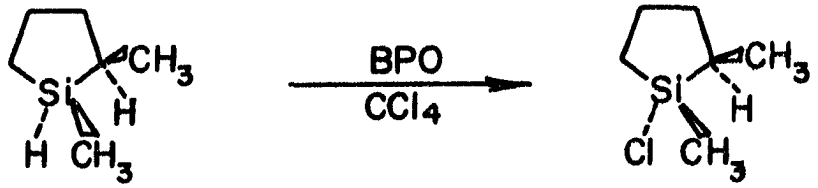
The compound 1-chloro-1,2-dimethylsilacyclopentane (15) was prepared by the method described for compound 14, except that methyltrichlorosilane was substituted for methyldichlorosilane (Equation 2-2).



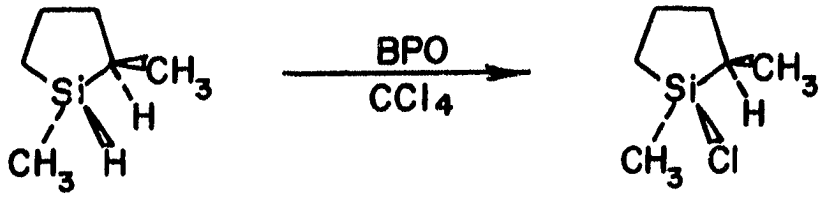
Equation 2-2

The isomers could not be separated by spinning band distillation; however, free radical chlorination of isomers 14a and 14b, catalyzed by benzoyl peroxide (BPO) gave isomers 15a and 15b stereospecifically (Equations 2-3 and 2-4). The free radical chlorination was greater than 95% stereospecific as determined by NMR spectra of the product mixtures. Stereospecific chlorination involving silyl free radical

intermediates have been reported in several studies[8,23] and all of

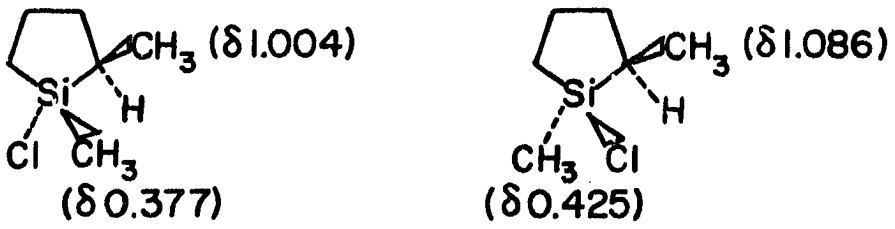


14A Equation 2-3 15A



14B Equation 2-4 15B

these reactions have given retention of configuration or racemization. There have been no examples of stereospecific inversion at a radical center. The NMR spectra of the silyl chloride isomers (Figure 2-2) agreed with the assignment of retention of configuration at Si for

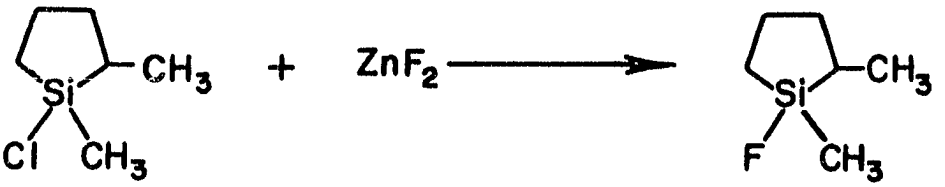


15A 15B

Figure 2-2. The proton chemical shifts were measured in CCl_4 with benzene as an internal reference and are reported in ppm downfield from TMS.

reactions 2-3 and 2-4. The Si-Me and C_2-Me groups of 15a are mutually shielding and the chemical shifts are upfield relative to the chemical shifts noted for 15b.

The compound, 1,2-dimethyl-1-fluorosilacyclopentane (16) was prepared by stirring ZnF_2 with silyl chloride (15) and then distilling the silyl fluoride (16) from the reaction mixture (Equation 2-5).



15 16

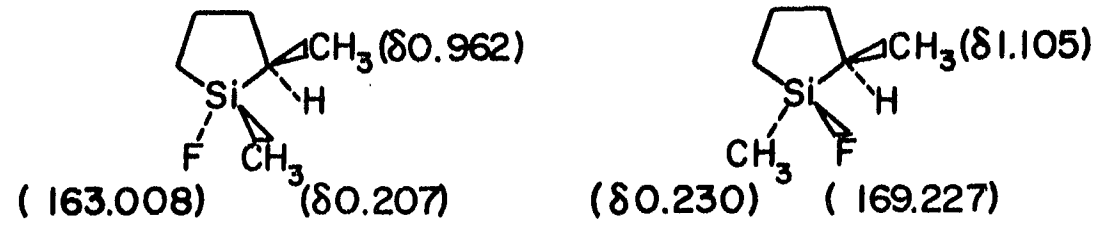
Equation 2-5

The reaction of the silyl chloride with ZnF_2 was not stereospecific. When a 20:80 mixture of 15a and 15b was reacted with ZnF_2, a 40:60 mixture of 16a and 16b was isolated. When the reaction was followed by NMR, rapid isomerization of the silyl chloride was observed with slower formation of the silyl fluoride. The silyl fluorides were, however, readily separable by spinning band distillation. Isomerization of an isomerically pure silyl fluoride by ZnF_2 was not observed even after heating for several hours.

The isomerization of the silyl chloride by ZnF_2 was probably caused by the presence of a small quantity of chloride ion giving an exchange reaction. As noted in the next chapter, only a very small quantity of chloride ion is required to cause rapid isomerization of the silyl chloride. Although no silyl fluoride formation was observed by NMR prior to isomerisation of the silyl chloride, it is possible that a small amount of silyl fluoride formed with the subsequent loss of chloride ion. The lack of isomerization in the case of the silyl fluoride is probably due to the fact that fluorine is a poor leaving group when

compared to chlorine. The fluorine-chlorine exchange reaction could simply be slow, or if the fluorine exchange reaction occurred by an S_Ni-Si mechanism, retention of configuration would result and no isomerization would be observed.

The silyl fluoride isomers 16a and 16b that were obtained by spinning band distillation were assigned structures in the manner previously used for the silyl hydride isomers 14a and 14b. ^{19}F NMR spectra aided in confirming the assignment of the structures.



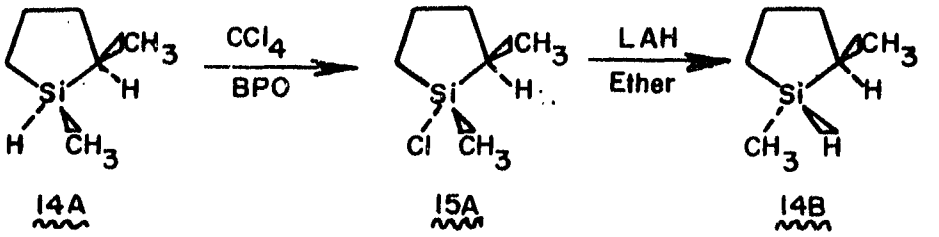
16A 16B

Figure 2-3. The proton chemical shifts were measured in CCl_4 with benzene as an internal standard and are reported in ppm downfield from TMS. The ^{19}F chemical shifts were measured in CCl_4 with $CFCl_3$ as a standard and are reported upfield relative to $CFCl_3$.

The lithium aluminum hydride (LAH) reduction of silyl chlorides normally occurs with inversion of configuration[3]; however, in ring-strained[7,8] or bicyclic systems[10], the reaction occurs by a retention mechanism. In acyclic systems, the LAH reduction has usually been considered to be a direct displacement of the S_N2-Si type[3]; however, recent evidence in the related displacement of chloride by Grignard reagents has been interpreted in terms of the slow formation of a pentacoordinate intermediate[5]. Either mechanism would require the silacyclopentane ring to span two equatorial positions in a trigonal bipyramidal intermediate, thus placing considerable strain on the ring system.

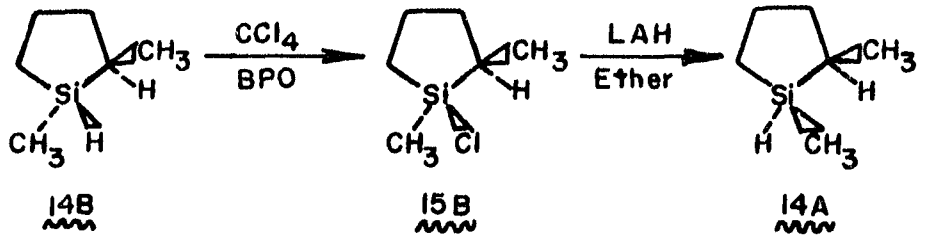
The silacyclobutane ring system cannot easily span two equatorial positions and, therefore; reacts by a retention mechanism in which the intermediate is presumably a trigonal bipyramid with the ring spanning an equatorial and an axial position.[8] Since the silacyclopentane ring is less strained than the silacyclobutane ring but has more strain than acyclic systems, it could presumably react by either a retention or inversion mechanism. The reaction stereochemistry of the LAH reduction of the silacyclopentane derivatives should prove useful in determining the amount of strain that is required to produce retention of configuration at Si.

Isomerically pure 1-chloro-1,2-dimethylsilacyclopentane was prepared by the free radical chlorination of one of the silyl hydride isomers as previously described in Equations 2-3 and 2-4. The silyl chloride was then reduced back to the hydride by reaction with LAH in ether to give the reaction stereochemistries noted in Equations 2-6 and 2-7.



14A 15A 14B

Equation 2-6



14B 15B 14A

Equation 2-7

As can be seen, the overall reaction sequence occurs with inversion of configuration. Since, as noted earlier, the free radical chlorination occurs with retention of configuration, the LAH reduction must occur with inversion of configuration at Si. This observation allows one to conclude that the silacyclopentane ring is capable of spanning two equatorial positions in a trigonal bipyramidal transition state (Figure 2-4); however, it is impossible to conclude whether or not a stable intermediate is formed in this reaction.

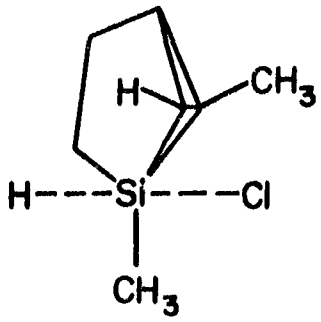
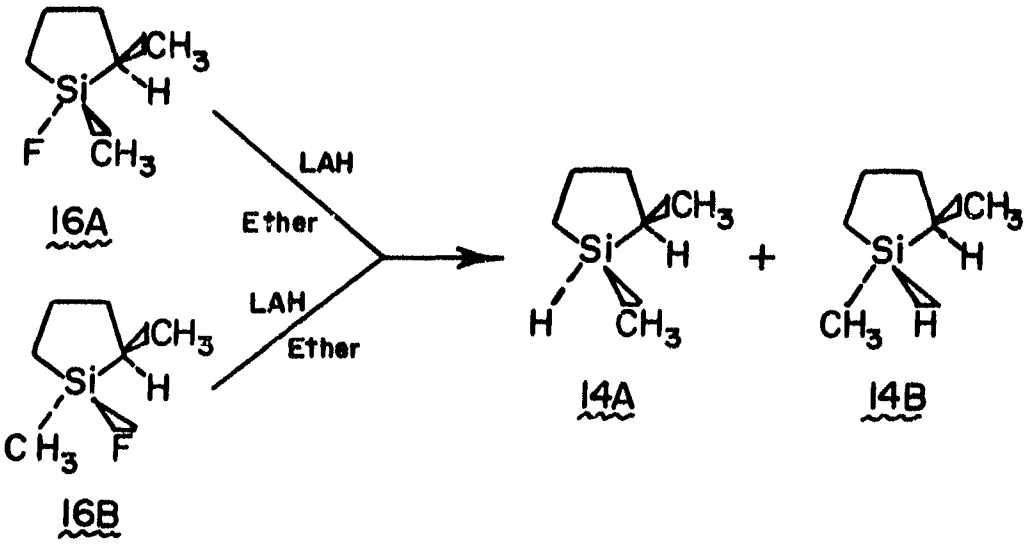


Figure 2-4

Fluorine, however, is a poorer leaving group than chlorine for reactions at Si, and detection of an intermediate in the preceeding reaction should be easier with fluorine as the leaving group. The pure isomers of 1,2-dimethyl-1-fluorosilacyclopentane were isolated by spinning band distillation. Reduction of mixtures containing a preponderance of either silyl fluoride isomer by LAH in ether resulted in a 50:50 ratio of 14a and 14b (Equation 2-8). When the reaction was followed by NMR, the 50:50 mixture of 14a and 14b was observed as soon as hydride formation was noted and the silyl fluoride isomeric ratio remained essentially unchanged during the course of the reaction. This indicates that the fluoride isomers are not isomerizing prior to

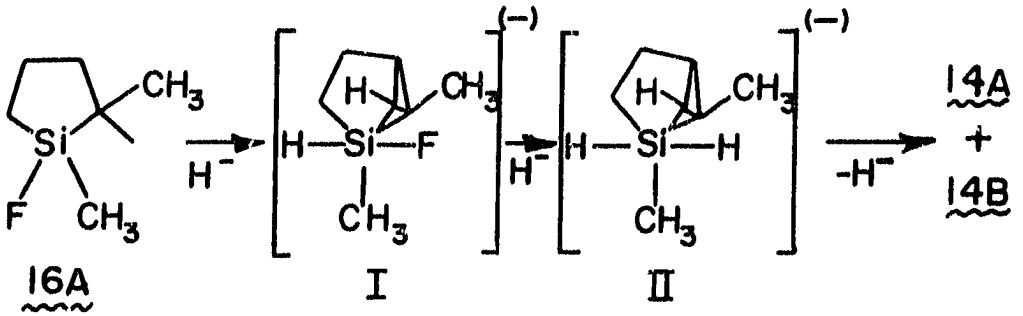
reaction. In order to test whether the silicon hydride was being



Equation 2-8

isomerized immediately upon formation, an extra amount of silyl hydride that was predominately one isomer was added to the reaction mixture. This excess hydride isomerized very slowly so that the initial formation of a 50:50 hydride mixture could not be explained by the immediate isomerization of the hydride. Presumably, the silyl hydride was isomerized during the reduction of the silyl fluoride. Corriu had previously reported the isolation of racemic silicon hydride from the LAH reduction of optically active silicon fluoride[25]; however; he did not propose a mechanism to account for the racemization. Several possible mechanisms could account for the formation of a 50:50 mixture of the hydride. One can imagine that the silicon fluoride reduction is occurring by competing retention and inversion pathways with fortuitously cancelling rates. This possibility does not seem likely since it would require the fortuitous identity of four rate constants. Furthermore, given the normal stability of silacyclopentanes toward

basic conditions, it is unlikely that reversible ring opening could cause the loss of stereochemical integrity. It is much more reasonable to assume that the silicon fluoride is converted irreversibly into a reaction intermediate which loses its configuration. A three-coordinate silyl cation can be ruled out because of the strength of the Si-F bond, the configurational stability of isomerically pure silicon fluoride in solution, and on other grounds as well[14]. Consequently, the intermediate is presumably one with expanded coordination at Si. One possible mechanism is illustrated in Equation 2-8. This mechanism



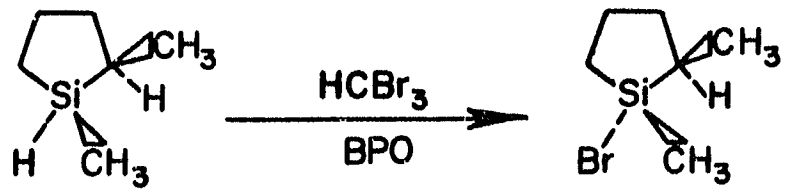
Equation 2-8

would require two moles of hydride, and there have been recent indications that some processes at Si may involve two moles of a nucleophilic reagent[26,27]. The relatively slow isomerization of silyl hydride by LAH in ether would presumably proceed through an intermediate analogous to intermediate II shown in Equation 2-8. It is also possible that the formation of pentacoordinate intermediate, I, followed by pseudorotation could account for the isomerization observed.

It may be the case that relatively subtle factors determine reaction pathways in organosilicon reactions. In reactions of silyl fluorides with diisobutylaluminum hydride, retention stereochemistry predominates in hexane as solvent while inversion is observed in ether solvent[4]. Even with lithium aluminum hydride, Sommer has previously

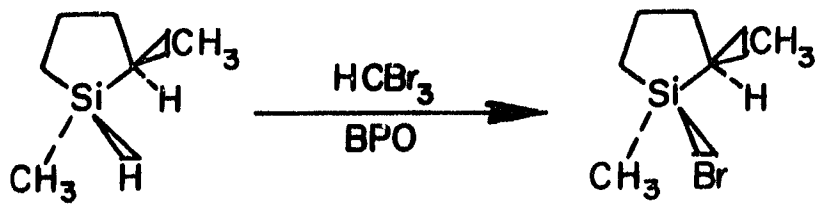
reported a stereospecific reduction of α-naphthylphenylmethylfluorosilane under conditions not obviously different from those employed in the preceeding study and by Corriu[25]. The relationships between stereochemistry and mechanisms of reactions at Si can, indeed, be quite complex, and further investigations are needed before definite conclusions can be made.

Since the studies of the fluoride, chloride, and hydride derivatives of the silacyclopentane system proved so fruitful, it was decided to continue these investigations by preparing the silyl bromide and p-anisyl derivatives. The isomers of 1-bromo-1,2-dimethylsilacyclopentane were prepared by free radical bromination of 14a and 14b (Equations 2-9 and



14A 17A

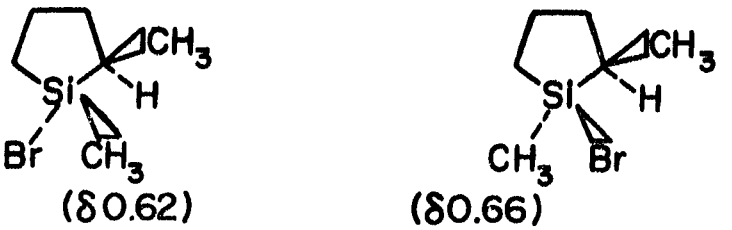
Equation 2-9



14B 17B

Equation 2-10

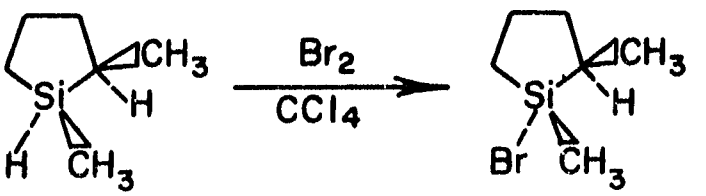
2-10). The NMR spectra aided in confirming the structural assignments (Figure 2-5).



17A 17B

Figure 2-5. Proton chemical shifts were measured in CCl_4 with TMS as a standard and are reported in ppm downfield from TMS.

The silyl bromide isomers, 17a and 17b, were also prepared stereospecifically with retention by the reaction of bromine in CCl_4 with the appropriate isomers of the silicon hydride (Equation 2-11).



14A 17A

Equation 2-11

Investigation of this reaction by Sommer[3] indicated that retention of configuration occurs due to the formation of an intermediate bromonium ion (Figure 2-6). The observation of retention of configuration for

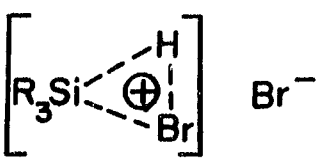
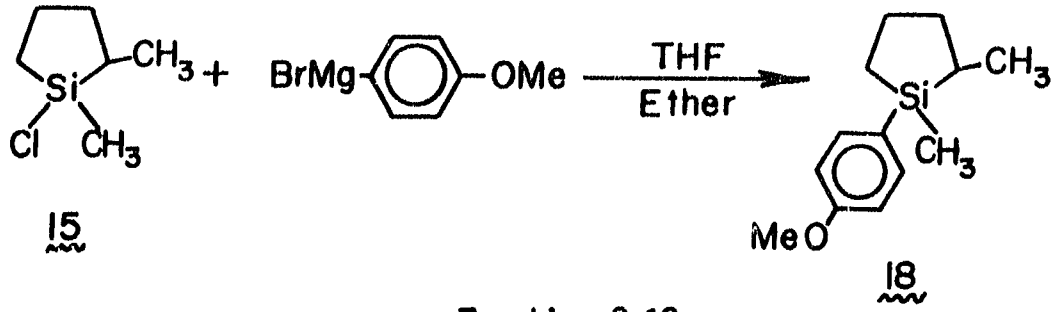


Figure 2-6

the silacyclopentane system tends to confirm Sommer's proposal.

The preparation of 1-(p-anisyl)-1,2-dimethylsilacyclopentane (18) proved to be more difficult than was originally anticipated. Attempts to prepare the p-anisyl derivative by addition of the p-anisyl Grignard reagent to silyl chloride, 15, failed even with prolonged heating. The difficulty was not in the preparation of the p-anisyl Grignard reagent but in the addition of the Grignard reagent to the silyl chloride. This result was surprising since other workers had no trouble in preparing either the acyclic derivative[28] or the silacyclobutane derivative[29]. Corriu reported, however, difficulty in reacting p-anisylmagnesium bromide with α-naphthylphenylmethoxymenthoxysilane and he noted that the addition of tetrahydrofuran (THF) aided in the formation of the anisyl derivative. Therefore, the reaction of p-anisylmagnesium bromide and 1-chloro-1,2-dimethylsilacyclopentane was repeated with the addition of THF after mixing of the reactants (Equation 2-12).

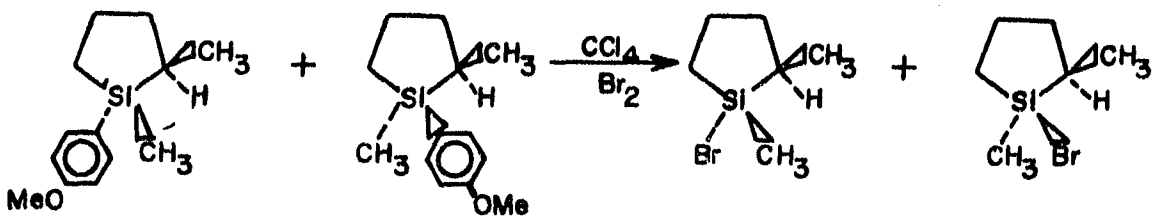


15 18

Equation 2-12

The reaction occurred when the THF was added; however, when the product was isolated, an NMR spectrum showed that the E-isomer had formed almost exclusively with only about 10% of the Z-isomer in the product mixture. Addition of bromine to the product mixture resulted in an 87:13 mixture of 17b and 17a respectively (Equation 2-13). Cleavage of the anisyl group from Si was the first reaction that was noted to proceed by inversion of configuration in the silacyclobutane ring system[29] so

presumably it would also occur by an inversion pathway in the silacyclopentane system.



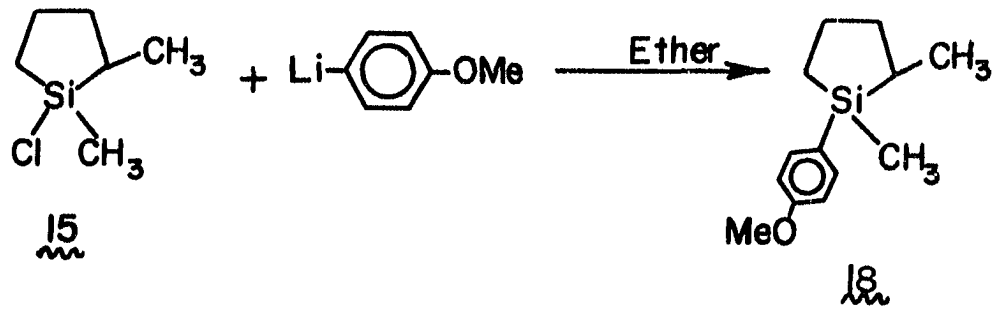
18A(90%) 18B(10%) 17A(13%) 17B(87%)

Equation 2-13

In order to study these reactions further, it was decided to attempt to prepare an equimolar mixture of 18a and 18b by other methods. Since the reaction with the silyl chloride was so difficult, it was hoped that reaction of p-anisylmagnesium bromide with the silyl bromide would occur easily without requiring the addition of THF and prolonged heating. A reaction occurred immediately upon addition of 1-bromo-1,2-dimethylsilacyclopentane to the Grignard reagent of p-bromoanisole in ether; however, none of the desired product was observed in the reaction mixture. About 50% of the product mixture was a mixture of anisole and 1,2-dimethylsilacyclopentane. The other 50% was an unidentified red solid that appeared to be polymeric. The reduction of a silyl bromide in low yield by Mg has been previously reported[30]; and a silyl Grignard reagent was proposed to account for this reduction. Formation of a silyl Grignard reagent is probably also responsible for the reduction observed in the present reaction.

Since using a more reactive silyl halide did not result in the desired product, use of a more reactive p-anisyl reagent was the next choice. Addition of 1-chloro-1,2-dimethylsilacyclopentane (15) to the

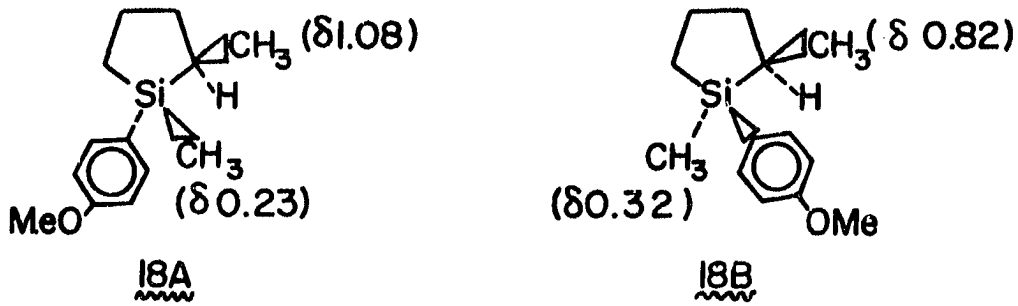
lithium reagent of p-bromoanisole in ether resulted in an immediate reaction. A NMR spectrum of the product mixture indicated that both isomers of the p-anisyl derivative had formed in about a 50:50 ratio (Equation 2-14). Addition of bromine in CCl_4 gave a 50:50 ratio of



15 18

Equation 2-14

17a and 17b. The isomers of product 18 were identified from their NMR spectra (Figure 2-7). The stereochemistry of the anisyl cleavage by bromine as previously noted, and the predominant formation of the most stable product in reaction 2-12 also aided in assigning the structures of 18a and 18b.



18A 18B

Figure 2-7. The proton NMR spectra were run in CCl_4 with TMS as a standard and were measured in ppm downfield from TMS.

As previously observed, the difficulty in forming 18 from silyl chloride and p-anisylmagnesium bromide in ether was very unusual. Corriu added phenyl-α-naphthylchloromenthoxysilane to p-anisylmagnesium bromide in ether and observed immediate formation of product with inversion of

configuration at Si[28]. Addition of 1-chloro-1,2-dimethylsilacyclobutane to p-anisylmagnesium bromide also resulted in immediate formation of the anisyl derivative; however, the reaction proceeded with retention of configuration.[29] The silacyclopentane system has approximately the same or less steric hindrance than the other systems described so steric hindrance must be ruled out as the main cause of the unique behavior observed. It is, however, possible that degree of angle strain plays an important role since the major difference in these systems lies in the degree of angle strain at Si.

As observed earlier in the LAH reduction of the silyl chloride, the angle strain in the silacyclopentane system is not sufficient to require a retention pathway where the ring would span an axial and equatorial site in a trigonal bipyramidal transition state. It is, however, possible that the angle strain in an S_N2-Si type transition state would be sufficient to cause a slow rate of attack by the entering nucleophile, and, therefore, a slower formation of the intermediate when the attacking species is bulky and a poorer nucleophile. The rapid reaction of the silyl chloride with LAH can be explained by the smaller size and greater nucleophilicity of the hydride ion, giving a more rapid formation of the S_N2 type intermediate and thus a faster reaction. The addition of THF to the silyl chloride-p-anisylmagnesium bromide system caused the insoluble Grignard reagent to dissolve, thus providing a more reactive solution. The THF may have also aided in solvating the positively charged Mg, thereby increasing the nucleophilicity of the p-anisyl group.

The stereochemistry of the reaction can be explained by the formation of a five-coordinate intermediate with sufficient lifetime to undergo pseudorotations to give the less sterically hindered product. As mentioned earlier, there is evidence that Grignard reactions that occur by inversion of configuration proceed via the slow formation of a five-coordinate intermediate.[5] Corriu observed that the rates of fluoride and chloride displacement by several Grignard reagents were essentially equal and concluded that bond breaking occurred in a fast step preceeded by the slower formation of an intermediate. It is, therefore, possible for an intermediate of this type to account for the stereochemistry observed in the silacyclopentane system.

Another likely mechanism involves the isomerization of silyl chloride prior to reaction. Formation of the less sterically hindered isomer would occur if there were a large enough difference in the rates of formation of the two isomers and the silyl chloride isomerization were faster than the rate of formation of the more sterically hindered isomer. The fact that silyl chloride does not isomerize in ether but does isomerize slowly in THF lends credence to this mechanism. The isomerization of the silyl chloride in THF is, however, fairly slow. When E-silyl chloride and THF are mixed in a 50:50 ratio, no isomerization is apparent after 2 hours; however, heating this mixture for about 6-8 hours at 60° gives complete isomerization. Since the Grignard reaction refluxes for one day after addition of THF, it is possible that this mechanism is operative.

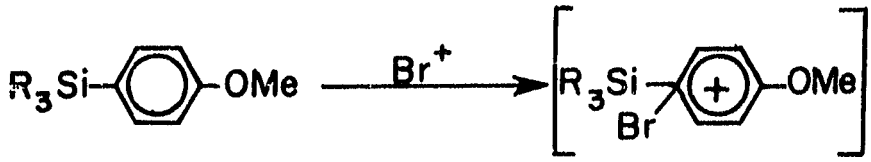
Both mechanisms require slow formation of Si-anisyl bond. Several observations indicate that the difficulties encountered in this reaction were caused by the entering rather than the

leaving group. Substitution of the more reactive silyl bromide did not result in formation of the desired product; however, use of the more nucleophilic lithium reagent resulted in product formation. These observations could be interpreted in terms of either of the proposed mechanisms.

There are also some points in each of the previously described mechanisms that are difficult to explain and must be investigated more fully before choosing between them. The mechanism involving initial isomerization by THF is based on the fact that isomerization by THF is fast compared to formation of the more sterically hindered isomer. It was noted earlier that isomerization by THF is fairly slow and unless the isomerization occurs faster under the reaction conditions or the formation of the more hindered isomer is extremely slow, reaction by this mechanism would not be likely. It is difficult to believe that the difference in reaction rates for the formation of the two isomers is very large since an equimolar mixture was formed fairly rapidly in the reaction with the lithium reagent. There is still the possibility that the isomerization of the silyl chloride occurs rapidly under the reaction conditions. As noted in the next chapter, several different agents can cause rapid isomerization of the chloride. Rapid isomerization of the chloride could possibly be detected by using isomerically pure silyl chloride as the starting material and isolating the unreacted silyl chloride before completion of the reaction.

In the mechanism involving pseudorotations of a five-coordinate intermediate, the slow loss of chloride ion is difficult to explain. In the reduction of the silyl chloride by LAH, the inversion stereochemistry indicates that Si-Cl bond breaking must have been faster than

pseudorotations and unless some type of electrophilic assistance to bond breaking was present in the reduction but not in the Grignard reaction, Si-Cl bond breaking for the Grignard reaction should have also been too rapid for pseudorotations to occur. Inversion of configuration was also noted for the reaction of the silacyclopentane anisyl derivative with bromine. The anisyl group is a very good leaving group in this reaction since the proposed mechanism involves initial attack of the phenyl ring by bromonium ion (Equation 2-15) followed by dis-



Equation 2-15

placement of p-bromoanisole by bromide.[31] Isomerization, however, occurred in the LAH reduction of the silyl fluoride. Fluoride is a poorer leaving group than chlorine in reactions at Si, but it is difficult to determine the type of leaving group required to produce an intermediate with a lifetime sufficient for pseudorotation to occur. Breaking of the Si-Cl bond in the Grignard reaction may, for some reason, be slower than previously observed for the LAH reduction allowing sufficient time for isomerization.

It is also possible that the size of the anisyl group caused pseudorotation to occur more rapidly. Immediately after attacking Si, the anisyl group would probably occupy an axial position in an S_N2 type intermediate. Since there is more steric hindrance in an axial position than in an equatorial position of a trigonal bipyramid, it is possible that the large anisyl group would quickly pseudorotate to the

less sterically hindered equatorial position before breaking of the Si-Cl bond could occur, thus causing isomerization of the final product. More data, however, is necessary before a definite conclusion can be reached. A study of the isomerization reactions at Si could aid in answering many of the questions posed in this study.

Chapter 2

Experimental Section

Preparation of 1,2-dimethylsilacyclopentane

Magnesium turnings (45 g, 1.8 moles) and 600 ml. anhydrous ether were placed in a round-bottom flask. The magnesium turnings were activated by the addition of 2 ml. of 1,2-dibromoethane. A solution of 1,4-dibromopentane (100g, 0.44 moles) and 600 ml anhydrous ether was added dropwise (two phases formed), then the reaction mixture was refluxed for 2 hours. The Grignard reagent was added dropwise to a solution of methyldichlorosilane (50.7 g, 0.44 moles) and 300 ml of anhydrous ether. The reaction mixture was stirred with a mechanical stirrer overnight, and then poured into a separatory funnel containing 75 g ammonium chloride and 600 ml cold water. The solution was separated, dried over anhydrous $MgSO_4$, and distilled to yield 24.3 g (48%) of a 50:50 mixture of 14a and 14b, b.p. 112-112.5°. The isomers were separated by spinning band distillation to give pure 14a and 14b: 14a- 100 MHz NMR (CCl_4, C_6H_6) δ0.055 (d, 3H, J=3.5 Hz), 0.15-1.95 (m, 10H), 1.035 (s), 4.01 (m, 1H); IR (neat): 2890, 2800, 2100, 1450, 1410, 1360, 1240, 1140, 1080, 1060, 1010, 980, 930, 880, 838, 810, 790, 728, 685 cm^{-1}. 14b- 100 MHz NMR (CCl_4,C_6H_6) δ0.13 (d, 3H, J=3.5 Hz), 0.2-2.0 (m, 10H), 1.07 (s), 3.83 (m, 1H); IR (neat): 2830, 2740, 2090, 1460, 1420, 1380, 1260, 1160, 1100, 1070, 1040, 1020, 994, 940, 891, 873, 840, 810, 770, 723 cm^{-1}. Mass Spectrum (m/e, rel. intensity) 114(26), 87(11), 86(100), 85(17), 72(47), 71(28), 59(26), 45(27), 44(24), 43(29). Anal. calculated for $C_6H_{14}Si$: C, 63.07; H, 12.35; Si, 24.58. Found: C, 62.98; H, 12.35; Si, 24.74.

Preparation of 1-chloro-1,2-dimethylsilacyclopentane

Magnesium turnings (45 g, 1.8 moles) and 500 ml anhydrous ether were placed in a round-bottomed flask. After activating the magnesium with 3 ml of 1,2-dibromoethane, a solution of 1,4-dibromopentane (102 g, 0.44 mole), methyltrichlorosilane (66 g, 0.44 mole) and 700 ml of anhydrous ether were added dropwise. The reaction mixture was refluxed for 2 days and then filtered under nitrogen. The resulting solution was distilled to remove the ether. The residue was vacuum distilled to yield 36 g (55%) of a 45:55 mixture of 15a and 15b, b.p. 95-96° (142 mm). NMR (CCl_4, C_6H_6): δ 0.4 (s), 0.42 (s), 1.05 (s), 2.7-2.0 (m); Mass Spectrum: (m/e, rel. intensity) 148(69), 122(84), 121(27), 120(40), 118(31), 117(56), 116(85), 115(100), 97(26), 95(23), 94(40), 93(56), 81(26), 80(36), 79(70), 78(91), 65(26), 63(55), 43(27), 41(24). Analysis calculated for $C_6H_{13}SiCl$: C, 48.46; H, 8.81; Si, 18.89. Found: C, 48.50; H, 8.78; Si, 18.97.

Preparation of 1,2-dimethyl-1-fluorosilacyclopentane

A 45:55 mixture of cis and trans-1-chloro-1,2-dimethylsilacyclopentane (40.23 g, 0.27 mole) and ZnF_2 (27.81 g, 0.27 mole) were placed in a round-bottomed flask equipped with a distillation head and a nitrogen inlet. The solution was stirred for 15 min and then distilled. Zinc fluoride, ZnF_2, (8.3 g, 0.08 mole) was added and the reaction mixture was distilled to yield 28 g (79%) of a 40:60 mixture of 16a and 16b, b.p. 110-111°. The isomers were separated by spinning band distillation. 16a- 100 MHz NMR (CCl_4, C_6H_6): δ 0.207 (d, 3H, J=7.6 Hz), 0.3-2.02 (m, 10H), 0.962 (d, J=1.5 Hz); ^{19}F NMR (CCl_4, $CFCl_3$) δ 163.008 (m). 16b- 100 MHz NMR (CCl_4, C_6H_6): δ 0.23 (d, 3H, J=7.6 Hz), 0.34-2.02 (m, 10H), 1.105 (d, J=7 Hz); ^{19}F NMR (CCl_4, $CFCl_3$) δ 169.227

(septet). Mass Spectrum (m/e, rel. intensity) 132(51), 104(99), 103(14), 91(22), 90(46), 89(100), 77(31), 76(31), 63(48), 62(49), 47(48), 32(44), 28(99). Anal. calcd. for $C_6H_{13}SiF$: C, 54.40; H, 9.95; Si, 21.24. Found: C, 54.40; H, 9.95; Si, 21.40.

A 20:80 mixture of 15a and 15b (0.38 g, 0.0026 mole) and ZnF_2 (0.154, 0.001 mole) were placed in a vial and heated at 78° C for 50 min. An NMR spectrum of the product mixture indicated that the chloride had completely isomerized but no product had formed. After heating for a total of 4 hr, an NMR spectrum showed that fluorosilane had formed in an equilibrium mixture (55:45 ratio of E to Z isomers).

A 20:80 mixture of 16a and 16b (0.115 g, 0.0011 mole) and ZnF_2 (0.18 g, 0.0014 mole) were placed in an NMR tube. The NMR tube was placed in an oil bath and held at 80°C for 3 hr. An NMR spectrum taken the following day showed no apparent isomerization.

Chlorination of 1,2-dimethylsilacyclopentane

A 29:71 mixture of 14a and 14b (5.86 g, 0.05 mole) was placed in a round-bottomed flask containing benzoyl peroxide (0.1 g, 0.0005 mole) and 15 ml dry CCl_4. The flask was equipped with a magnetic stirrer, a reflux condenser, and a nitrogen inlet system. The reaction mixture was heated in an oil bath held at 82° for 1.5 hr. Most of the CCl_4 was then removed by distillation. The residue was vacuum distilled to yield 7.62 g (54.6%) of a 30:70 mixture of 15a and 15b, b.p. 65° (44mm). 15a- 100 MHz NMR (CCl_4, C_6H_6): δ 0.377 (s,3H), 0.4-2.04 (m, 10H), 1.004 (s). 15b- 100 MHz NMR (CCl_4,C_6H_6): δ 0.425 (s, 3H), 0.54-2.05 (m, 10H), 1.086 (d, J=6.8 Hz).

Reduction of 1-chloro-1,2-dimethylsilacyclopentane

A 30:70 mixture of 15a and 15b (0.38 g, 0.0026 mole), lithium aluminum hydride (0.03025 g, 0.0008 mole), and 2 ml dry ether were placed in a vial equipped with a septum. A GLPC trace was obtained immediately after mixing. GLPC analysis (16' x 1/8" column, 15% Apiezon L on 60-80 mesh Chromosorb W; 115° isothermal) showed that two products had formed with retention times* (min) of 2.82 (33.8%) and 3.44 (66.2%). By GC-MS analysis and comparison of the retention times to pure 14a and 14b (3.40 and 2.76 respectively), the products were identified as 14b and 14a respectively.

A 76:24 mixture of 15a and 15b was treated in the previous manner. A GLPC trace showed that the two products had formed. A comparison of retention times indicated that 14a and 14b had formed in a ratio of 24.1:75.9 respectively. GLPC traces obtained after allowing the reaction mixture to sit showed that the silicon hydride slowly isomerized. After 1 day the isomerization was complete.

Reduction of 1,2-dimethyl-1-fluorosilacyclopentane

A 95:5 mixture of 16a and 16b (0.27 g, 0.002 mole), lithium aluminum hydride (0.03 g, 0.0008 mole), and 2 ml anhydrous ether were placed in vial equipped with a septum. The reaction mixture was immediately analyzed by GLPC (16' x 1/8" column of 15% Apiezon L on 60-80 mesh Chromosorb W; 115° isothermal). Three peaks were observed with retention times of 2.44 (38.95%), 2.74 (34.33%), and 3.38 (26.72%), and GC-MS analysis and a comparison of retention times showed that the peaks could be assigned to unreacted starting material, 14b, and 14a respect-

*The retention times were measured from the ether signal.

ively. A 44:56 ratio of 14a to 14b was observed.

The preceeding reaction was repeated using 30:70, 50:50, and 77:23 ratios of 16a to 16b. GLPC analyses of the reaction mixtures gave 14a to 14b ratios of 47:53, 45:55, and 49:51 respectively.

The reduction of the fluorosilane was repeated using the procedure previously described except 0.15 ml of a 80:20 mixture of 14a and 14b was added to the reaction mixture. A GLPC analysis of the reaction mixture showed a 67:33 mixture of 14a and 14b had formed. The products slowly isomerized, giving a Z:E ratio of 52:48 after about 1 day. After obtaining the GLPC trace, nitrogen was bubbled through the sample to remove most of the ether and the remaining solution was dissolved in CCl_4. An NMR spectrum indicated that the unreacted starting material had not isomerized.

Free Radical Bromination of 1,2-dimethylsilacyclopentane

trans-1,2-Dimethylsilacyclopentane, 14b (0.102 g, 0.0009 mole) and 0.5 ml Br_3CH were placed in an NMR tube with some benzoyl peroxide. The reaction mixture was heated to 80° for 10 min. An NMR showed exclusive formation of trans-1-bromo-1,2-dimethylsilacyclopentane, 17b. NMR (CCl_4, TMS): δ 0.66 (s, 3H), 0.8-2.0 (m), 1.04 (broad doublet). The preceeding reaction was repeated using a mixture of hydrides that was predominately cis. An NMR showed formation of a mixture of bromides that was predominately cis. NMR (CCl_4,TMS): δ 0.62 (s, 3H), 0.7-2.0 (m), 1.07 (broad doublet).

Preparation of 1-bromo-1,2-dimethylsilacyclopentane from 1,2-dimethylsilacyclopentane

1,2-Dimethylsilacyclopentane, 14 (12 g, 0.11 moles) and 25 ml CCl_4

were placed in a round bottomed flask. Bromine (16.89 g, 0.11 moles) and 20 ml CCl_4 were added slowly to the reaction mixture which was cooled in an ice bath. The CCl_4 was removed by vacuum distillation. The residue was vacuum distilled to yield 13.66 g (67%) of the desired product, b.p. 63-64° (15 mm). 100 MHz NMR (CCl_4, C_6H_6): δ 0.54 (s, 3H), 0.58 (s, 3H), 0.7-2.1 (m, 20H), 0.9 (d, J=7Hz), 1.12 (d, 7Hz); Mass spectrum m/e (rel intensity) 194(41), 192(41), 166(100), 164(100), 152 (37), 151(44), 150(37), 149(37), 138(26), 136(26), 125(55), 124(39), 123(56), 122(37), 109(34), 107(31), 97(28), 85(29), 58(27), 41(21). Anal. calcd. for $C_6H_{13}SiBr$: C, 37.31; H, 6.78; Si, 14.54. Found: C, 37.26; H, 6.72; Si, 14.56.

trans-1,2-Dimethylsilacyclopentane (0.44 g, 0.0004 mole) and 0.3 ml CCl_4 were placed in an NMR tube and 0.3 ml of 1M Br/CCl_4 was added. An NMR taken immediately after addition of the bromine showed that a 92:8 mixture of trans:cis 1-bromo-1,2-dimethylsilacyclopentane had formed. This reaction was repeated using a mixture of 1,2-dimethyl-silacyclopentanes in which the cis isomer predominated. An NMR taken immediately after addition of the bromine showed a mixture of 1-bromo-1,2-dimethylsilacyclopentanes in which the cis isomer predominated.

Preparation of cis-1-(p-anisole)-1,2-dimethylsilacyclopentane

Magnesium turnings (10g, 0.4 mole) and 300 ml ether were placed in a round bottomed flask. The Mg was activated by the addition of 1 ml 1,2-dibromoethane. p-Bromoanisole (43g, 0.23 mole) in 150 ml ether was added dropwise. The reaction mixture was stirred for 1 hr after addition was complete. The Grignard reagent was added to 1-chloro-1,2-dimethyl-silacyclopentane (29g, 0.2 mole) in 150 ml ether. The reaction mixture

was heated for approximately 18 hr then 200 ml THF was added and the solution was heated overnight. The reaction was then hydrolyzed with an aqueous solution of NH_4Cl, the ether was removed, and the residue was vacuum distilled to give 14g (31%) of a product mixture that contained greater than 90% of 18a, b.p. 96° (0.9mm). NMR(CCl_4): δ 0.23 (s, 3H), 1.08 (s), 0.7-2.1 (m, 10H), 3.74 (s, 3H), 6.7-6.9 (d, 2H), 7.28-7.53 (d, 2H).

Preparation of 1-(p-anisole)-1,2-dimethylsilacyclopentane from the Lithium reagent

Lithium wire (1.4g, 0.2 mole) and 160 ml ether were placed in a round-bottomed flask. A solution of p-bromoanisole (18.8 g, 0.1 mole) and 60 ml ether was added slowly. After addition was complete, the lithium reagent was filtered into a round-bottomed flask. 1-Chloro-1,2-dimethylsilacyclopentane (10g, 0.07 mole) and 50 ml ether was added slowly. The reaction mixture was hydrolyzed with an aqueous solution of NH_4Cl. The ether was removed with a rotary evaporator. The residue was vacuum distilled to give 9g (61%) of the desired product, b.p. 86-87° (0.25 mm). NMR (CCl_4): δ 0.25 (s, 3H), 0.32 (s, 3H), 0.5-2.1 (m, 20H), 0.82(s), 1.05 (s), 3.65 (s, 6H), 6.0-7.82 (m, 4H), 7.2-7.42 (m, 4H); IR(neat): 2950, 2880, 1600, 1580, 1500, 1460, 1310, 1280, 1250, 1180, 1120, 1090, 1040, 1020, 826, 812, 782, 763, 742 cm^{-1}; Mass Spectrum m/e (rel intensity); 220(3), 205(2), 164(2), 151(5), 150(3), 135(3), 112(2), 108(2), 97(3), 59(11), 58(100), 57(9), 55(3), 53(3), 45(3), 44 (22), 43(98), 42(51), 41(17), 39(27), 38(15), 37(13), 36(3). Anal. calcd. for $C_{13}H_{20}SiO$: C, 70.85; H, 9.15; Si, 12.75. Found: C, 70.59; H, 8.98; Si, 13.01.

Addition of Bromine to 1-(p-anisole)-1,2-dimethylsilacyclopentane

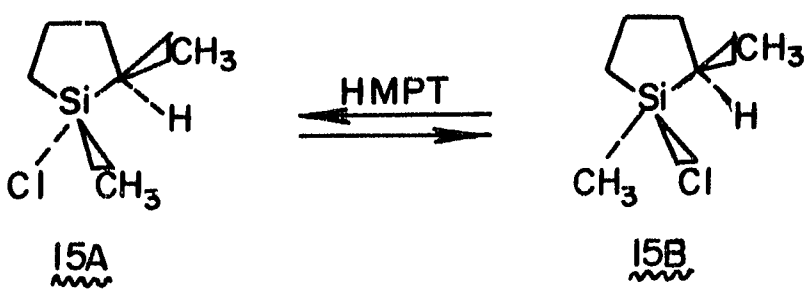
The 1-(p-anisole)-1,2-dimethylsilacyclopentane (0.0716g, 0.0003 mole) that was prepared from the lithium reagent was placed in an NMR tube with 0.1 ml CCl_4. Bromine (0.2 ml of a 1M solution in CCl_4) was added. An NMR taken immediately after addition showed a 50:50 mixture of cis- and trans-1-bromo-1,2-dimethylsilacyclopentane.

E-1-(p-anisyl)-1,2-dimethylsilacyclopentane, 18a (0.14g, 0.0006 mole) that was prepared from the Grignard reagent was placed in an NMR tube with 0.2 ml CCl_4. Bromine (0.4 ml of a 1M solution in CCl_4) was added. An NMR taken immediately after addition showed an 87:13 ratio of trans- to cis-1-bromo-1,2-dimethylsilacyclopentane after 86% conversion of the starting material. HMPT (0.3 ml of a 1 x 10^{-2}M solution in CCl_4) was added to the reaction mixture to give a 50:50 mixture of bromides.

Chapter 3

Since all of the solvent induced isomerizations of asymmetric silanes have been proposed to occur through the formation of extra-coordinate species, a study of the isomerizations of silacyclopentane derivatives would hopefully aid in explaining the mechanisms of the isomerizations that occurred in some of the reactions presented in the preceeding chapter. Investigations of the silacyclopentane isomerizations would also be helpful in determining the mechanism of isomerization at Si since an intermediately strained ring system has not been previously studied. Different reaction kinetics were observed for Corriu's acyclic system[15] and the silacyclobutane system[29]; therefore the silacyclopentane system would aid in determining the degree of angle strain needed to produce a certain mechanism.

The rates of the isomerization of E-1-chloro-1,2-dimethylsilacyclopentane (15a) by various concentrations of HMPT (Equation 3-1) were obtained by measuring the isomerization of the E-isomer with time (see Experimental Section for detailed explanation). The rate of



15A 15B

Equation 3-1

isomerization of the E-isomer was measured by the repeated integration of the Si-Me peaks of 15a and 15b in the NMR spectrum at definite time intervals. The observed rate constant k_{obs} is given by Equation 3-2.[32]

$$-dE/dt = k_{obs}\,[HMPT]^x[SiCl]^y$$

Equation 3-2

Since HMPT is present in only catalytic amounts and remains constant during the course of the isomerization, k_{obs} can be obtained from Equation 3-3 where A_o is the original concentration of the E-isomer, A_e is the concentration at equilibrium, and A is the concentration at time t.[32] A plot of $\ln (A_o-A_e)/(A-A_e)$ versus t has a slope equal to k_{obs}.

$$\ln\left[\frac{A_o - A_e}{A - A_e}\right] = k_{obs}\,t$$

Equation 3-3

A straight line plot was obtained when the preceeding graph was plotted for the isomerization of 15a by HMPT, thus indicating that the isomerization has a first order dependence on chlorosilane.

Since the isomerization of 15a is an equilibrium reaction, k_{obs} equals the sum of the forward and reverse rate constants. The forward rate constant, k_f, can be calculated from the value of k_{obs} and the equilibrium concentrations of the E and Z isomers. The dependence on HMPT of the isomerization was obtained by measuring the rate of isomerization of 15a at several different HMPT concentrations. Since the overall concentration of silyl chloride remained constant, the order in HMPT could be obtained from Equation 3-4, where x is the order in HMPT.

$$k_f = k_{1+x}\,[HMPT]^x$$

Equation 3-4

A graph of log k_f versus [HMPT] gave a 1.5 order dependence on HMPT. Since this order is not a whole number, the mechanism could not be as simple as had been previously thought. The simplest mechanisms involving a fractional order in HMPT would be one with pathways that have a first and second order dependence on HMPT; thus, the equation for k_f would include a first and a second order term (Equation 3-5).

$$k_f = k_2 [HMPT] + k_3[HMPT]^2$$

Equation 3-5

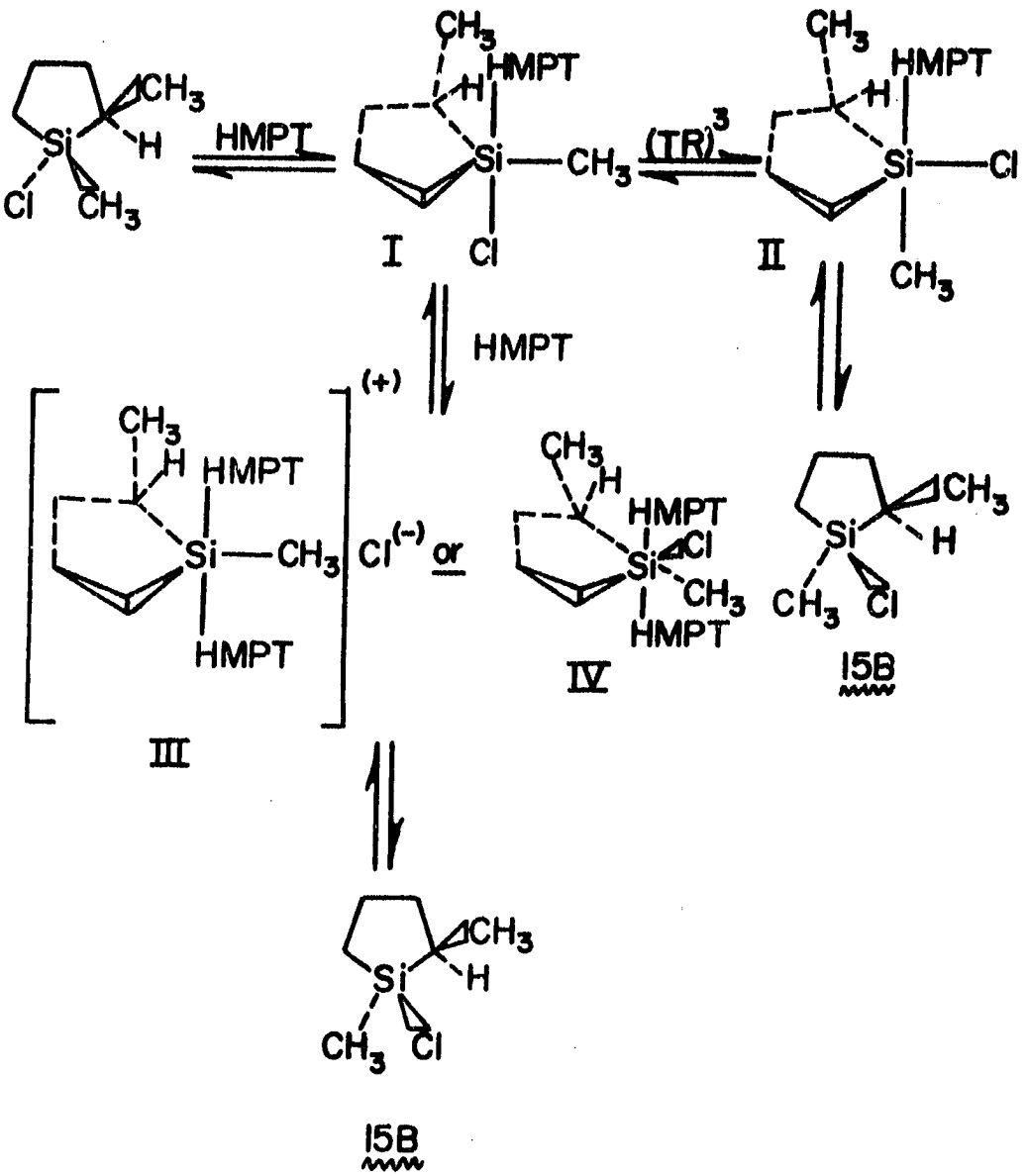
From this equation, it is obvious that a straight line graph should be obtained from a plot of $k_f/[HMPT]$ versus [HMPT]. When the k_f values from the isomerization of 15a by HMPT were plotted in this manner, a straight line was obtained, thus, the rate equation for this isomerization can be described by Equation 3-6. The values of k_2 and

$$-dE/dt = k_2[SiCl][HMPT] + k_3[SiCl][HMPT]^2$$

Equation 3-6

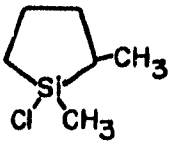
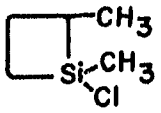
k_3 were obtained from the intercept and slope of the preceeding graph giving values of 0.014 $M^{-1}sec^{-1}$ and 28.82 $M^{2}sec^{-1}$ respectively. The isomerization of the silyl chloride can, therefore, occur by two different pathways as illustrated in Equation 3-7. The formation of intermediate I can either be followed by pseudorotations to give isomerization or by addition of another molecule of HMPT to give structure III or IV as proposed by Corriu for the isomerization of the acyclic system.[15]

The activation parameters, E_a, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ were obtained in the usual manner from the equation, $k = A \exp[-E_a/RT]$, by plotting ln k_f versus 1/T. The rate of isomerization of 15a by 5×10^{-3} M HMPT in CCl_4



Equation 3-7

was measured at various temperatures to give the values of k_f used in the graph (see experimental section for further details). The values of E_a, ΔH^*, and ΔS^* for the isomerization of 15a by HMPT are 6.15 kcal/mole, 5.54 kcal/mole, and -55 cal/mole°K, respectively. In Table 3-1 these values are compared to those reported for other systems. As can

R	ΔH^*(kcal/mole)	ΔS^*(cal/mole°K)
	5.54	-54.9
	10.5	-40
l-PrPh-l-NpSiCl	3.15	-55
EtPh-l-NpSiCl	0.39	-57
(OMent)(p-MeOPh)-l-NpSiCl	0.5	-62

[a] see Reference 29

[b] see Reference 15

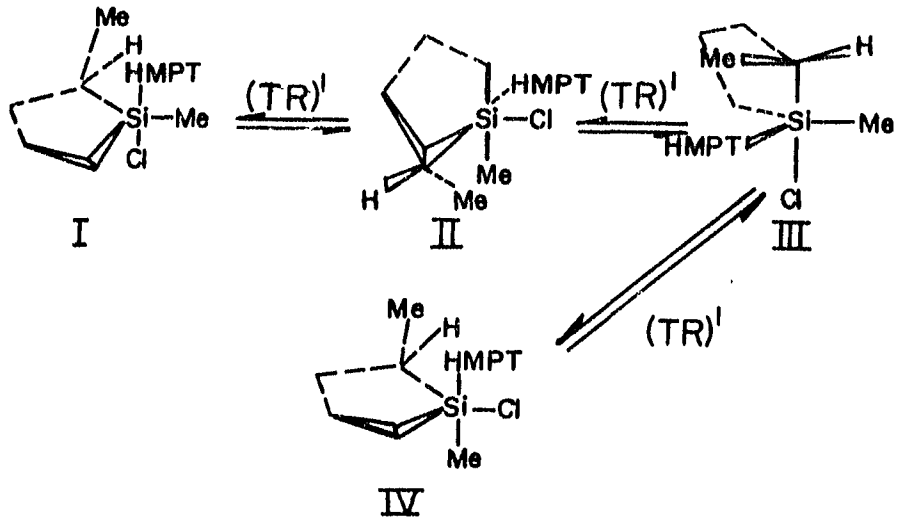
Table 3-1

be seen from Table 3-1, the values for silacyclopentane lie in between those for the silacyclobutane and acyclic systems. In general, ΔH^* is seen to increase with angle strain, while ΔS^* decreases with increasing angle strain. Comparisons of this type may not be valid since somewhat different mechanisms were proposed for the acyclic and silacyclobutane systems[15,29]; however, it is possible that some information may be gained in this manner.

A comparison of the rates of isomerization of various silyl chlorides by HMPT gave the order: silacyclobutane>silacyclopentane> acyclic. At 1 x 10^{-3}M HMPT in CCl_4 the silacyclobutane isomerization is 150 times faster than the silacyclopentane isomerization; however, since the apparent order of the silacyclobutane isomerization changes with HMPT concentration, the relative values of k_f may differ at other HMPT concentrations. Corriu used much larger HMPT concentrations to measure the rates of isomerization in his systems than were used in either the silacyclobutane or the silacyclopentane systems. His isomerizations must, therefore, occur at a much slower rate than those observed for the cyclic systems. This difference in rate must be at least partially due to steric hindrance since Corriu's systems are much more sterically hindered than the other systems studied.

The mechanisms of both the acyclic and silacyclobutane systems involve the addition of 2 moles of HMPT before isomerization occurs. The difference in these mechanisms lies in the fact that the acyclic system obeys third order kinetics throughout the range it was studied; while the silacyclobutane system shows third order kinetics at low concentrations of HMPT and second order kinetics at higher concentrations of HMPT. In the silacyclobutane system, there is a change in the rate determining step such that attack by the first HMPT molecule is rate determining at higher HMPT concentrations, while addition of the second molecule of HMPT is slower for low HMPT concentrations.[29] The mechanism of the silacyclopentane system differs from both the acyclic and silacyclobutane systems since a large portion of the isomerization occurs through an intermediate containing just one molecule of HMPT. This seems to indicate that the trigonal bipyramidal intermediates of the

silacyclopentane system are unusually stable allowing the triple turnstile rotation[33] shown in Equation 3-8. It is, however, difficult to



Equation 3-8

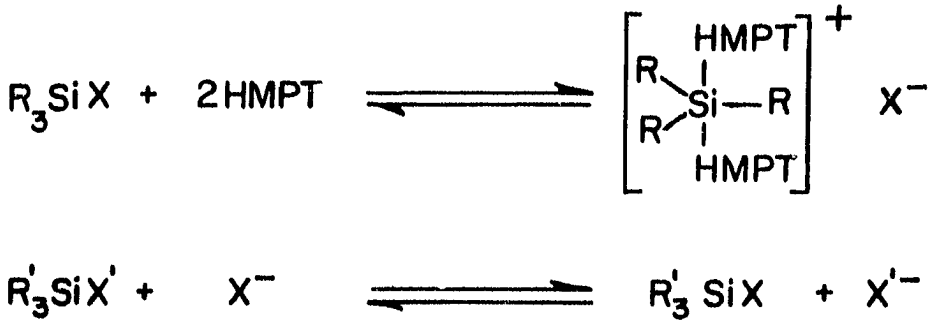
believe that intermediates I-IV are particularly stable. Intermediates I and IV involve angle strain since the normal C-Si-C angle is expanded to 120°. The structures of II and III are also energetically unfavorable due to compression of the C-Si-C angle and the placement of the more electronegative substituents in the equatorial positions. Investigations in phosphorus chemistry have indicated that electronegative substituents tend to occupy the axial positions in a trigonal bipyramidal intermediate and energy is required to force them into an equatorial position.[13,17,18] Since all of the structures of intermediates I-IV are energetically unfavorable, it is possible that the behavior of the silacyclopentane system is due to extremely rapid pseudorotations between structures that are approximately equivalent in energy rather than an unusual stability of the trigonal bipyramidal structure. This possibility is not unlikely since rapid pseudorotations were observed for the SiF_5^- anion where all of the possible trigonal bipyramidal structures are equivalent.[27] Rapid pseudorotations would not be readily observed

in the silacyclobutane system since intermediates II and III would be much more energetically favorable than the other structures involved. Intermediates I and IV would be much more favorable for the acyclic system, so here again rapid pseudorotation would not be likely to occur. The observation of first order rate dependence on HMPT can therefore be explained by rapid pseudorotation of structure I (Figure 3-8) followed by loss of HMPT to give the more stable tetrahedral structure of the product before attack by a second molecule of HMPT can occur. This mechanism could also acccunt for the higher value of $\Delta H^{\ddagger}$ observed for the silacyclopentane isomerization as compared to the values obtained for the acyclic systems (Table 3-1), since more energy would be required to form intermediate I (Equation 3-8) than would be required to form the analogous acyclic intermediate.

Rapid pseudorotation could also possibly account for the isomerizations observed in the LAH reduction of silyl fluoride, 16, and in the Grignard formation of anisyl derivative, 18. Attack of the entering group in these nucleophilic displacements would give a structure analogous to intermediate I (Figure 3-8). If bond breaking did not immediately occur, pseudorotations could cause isomerization. The mechanisms of the nucleophilic displacements that occurred with inversion (Chapter 2) possibly involve a transition state with nearly simultaneous bond breaking and making rather than the actual formation of an intermediate.

The mechanism of the third order pathway for the isomerization of 15a is probably similar to the mechanism proposed by Corriu for the racemization of the acyclic system. This pathway could involve formation of either intermediate III or IV as illustrated in Equation 3-7. In order to determine which intermediate was more likely, 1-bromo-1,2-di-

methylsilacyclobutane and 1-chloro-1,2-dimethylsilacyclopentane were mixed to see if halide-halide exchange would occur in the presence of HMPT. With the addition of 5×10^{-3}M HMPT in CCl_4, rapid halide-halide exchange occurred; however, no exchange was noted in the presence of CCl_4 alone. This exchange indicates that ionization of the Si-halide bond does occur in at least one of the systems involved; however, exchange may be caused by nucleophilic displacement in the other system (Equation 3-9).



Equation 3-9

It was decided to continue the investigation of the isomerization of the silacyclopentane system by studying other isomerizing agents and other silacyclopentane derivatives. The silyl chloride isomer, 15a, is isomerized by several compounds other than HMPT. Tetraalkylammonium salts give rapid isomerization of the silicon chloride derivative. The isomerization by relatively small amounts of n-Bu_4NF, n-Pr_4NCl, or n-Bu_4NBr was so fast that the Si-Me peaks of isomers 15a and 15b coalesced to one peak in NMR spectra. The rate of isomerization of silyl chloride by 2.6×10^{-5}M n-Bu_4NBr in CCl_4 was measured and found to occur at a rate 10^4 times faster than that observed for the HMPT isomerization. This isomerization was also about 100 times faster than that observed for the isomerization of 1-chloro-1,2-dimethylsilacyclobutane by n-Bu_4NBr.

The rapidity of this isomerization is in part due to the greater nucleophilicity of halide ion as compared to HMPT. The halide ion being more nucleophilic would attack the Si faster, giving faster formation of the intermediate. In the isomerization of halide ion, there is also the possibility of a direct displacement reaction involving an S_n2 type intermediate. A direct displacement of halide ion by halide ion would result in inversion of configuration at Si, thereby giving a rapid rate of isomerization. Addition of pyridine or DMSO in CCl_4 also gave rapid isomerization of the chloride; however, some sort of reaction must have occurred in both of these cases since the solution became cloudy after the addition of these compounds. Sulfolane and THF gave slower isomerizations and heating was required to speed up the isomerization.

The rate of isomerization of the 1,2-dimethyl-1-fluorosilacyclopentane (16) could not be accurately measured since the Si-Me peaks of isomers 16a and 16b were too close in the NMR spectrum for accurate integration; however, the relative rates of isomerization by various agents could be observed by the change in the Si-Me peak heights. The isomerization of silyl fluoride by HMPT occurred much slower than the corresponding isomerization of the silyl chloride. A 5×10^{-3} M solution of HMPT in CCl_4 gave no apparent isomerization of the silyl fluoride after four days as compared to almost complete isomerization of the silyl chloride in 15 minutes. Larger concentrations of HMPT, did, however, cause isomerization of the silyl fluoride. A 3:7 molar ratio of HMPT to silyl fluoride caused about half of the silyl fluoride to isomerize in about 2 days.

All of the alkylammonium salts tested (F^-, Cl^-, Br^-) gave rapid isomerization of the silyl chloride; however, an equivalent quantity of n-Bu_4NF gave much slower isomerization of silyl fluoride and with n-Pr_4NCl, no apparent isomerization of the silyl fluoride was observed unless very large quantities of the salt were used. Rapid isomerization of the silyl fluoride occurs if it is dissolved in pure methanol; however, a 3:1 ratio of methanol to silyl fluoride in CCl_4 is not completely isomerized after 2 days. This implies that there is a large order in methanol for this isomerization. Sommer observed about third order dependence on methanol for the isomerization of his acyclic fluoride.[34] The mechanism he proposed involved addition of one mole of methanol to give a five-coordinate intermediate which caused isomerization and the other molecules of methanol were used to solvate this intermediate. A similar mechanism is probably operative in the silacyclopentane system. Other solvents also caused isomerization of the silyl fluoride. A 1:1 mixture of DMF to silyl fluoride gave isomerization of half of the silyl fluoride in less than 2 hours; however, complete isomerization never did occur, indicating that some sort of reaction of the DMF must have occurred. The addition of DMSO gave very slow isomerization of the fluoride with only partial isomerization after 3 days.

The silyl hydride was much more difficult to isomerize than the previously studied halides. No isomerization of 1,2-dimethylsilacyclopentane by n-Bu_4NF was noted after 6 days. The silacyclobutane hydride was isomerized rapidly by cyanide ion in DMF, and the isomerization became extremely rapid if a small amount of water was added to the DMF.[29] The silacyclopentane derivative isomerized much more slowly under similar conditions giving only partial isomerization after one

day as compared to complete isomerization of the silacyclobutane system in less than 10 minutes. This difference in rates is probably due to the slower formation of the silacyclopentane intermediate as observed with the isomerization of the silyl chloride by HMPT.

The nature of the silacyclopentane derivative seemed to be the major factor determining the ease of isomerization at Si. The order of increasing ease of isomerization is H<F<Cl<Br. Isomerization of the silyl bromide derivative began as soon as it was formed stereoselectively, making it difficult to isolate an isomerically pure product, whereas isomerization of the hydride occurred only when the extremely nucleophilic cyanide ion was added. The order noted for the ease of isomerization follows the order of increasing leaving group ability. This fact could partially account for the large differences in rate between the silyl chloride and fluoride since a good leaving group could give formation of a siliconium ion like intermediate III in Figure 3-7. If the siliconium ion actually accounts for the third order isomerization of silyl chloride by HMPT, a slower rate for the silyl fluoride would be expected since this mechanism is not likely to occur for the silyl fluoride and hydride.

Another factor in determining the ease of isomerization of the silacyclopentane derivatives is the nucleophilicity of the solvent. The silyl chloride was rapidly isomerized by the fluoride, chloride, and bromide alkylammonium salts, while with the silyl fluoride, only the fluoride salt gave a moderate rate of isomerization, and the silyl hydride was not even isomerized by the fluoride salt. The rate of isomerization must then depend, to some extent, on the rate of formation of the pentacoordinate intermediate. This fact could explain the

difference in reactivity between silyl fluoride and hydride, since fluoride is more electron withdrawing than hydride and would therefore make the Si more electropositive and thus more susceptible to nucleophilic attack.

Chapter 3

Experimental Section

Kinetic Measurements

E-1-Chloro-1,2-dimethylsilacyclopentane was prepared stereospecifically from 1,2-dimethylsilacyclopentane as previously described. Solutions of 1.81M cis-1-chloro-1,2-dimethylsilacyclopentane in CCl_4; HMPT of varying concentrations in CCl_4 and 5.2×10^{-5}M n-Bu_4NBr in CCl_4 were prepared.

In a typical run, 0.5 ml of the cis-1-chloro-1,2-dimethylsilacyclopentane solution was placed in an NMR tube. The NMR tube was placed in the cavity of the A60A NMR Spectrometer for about 5 min. to allow the solution to thermally equilibrate. The temperature of the NMR cavity was determined by using the chemical shifts of ethylene glycol or methanol as standards. After equilibration, a 0.5 ml aliquot of the isomerizing agent was added. The rate of isomerization of the silyl chloride was followed by integrating the Si-Me peaks of the E and Z chlorides at definite time intervals. The peaks were integrated by using a 100 Hz sweep width and a 100 sec sweep time.

The rate of the isomerization is given by the following equation where k_{obs} is the observed rate constant, [HMPT] and [SiCl] are the concentrations of HMPT and silyl chloride, and x and y are the orders in HMPT and silyl chloride respectively.

$$-dE/dt = k_{x+y}[HMPT]^x[SiCl]^y$$

Since the HMPT acts as a catalyst and its concentration remains constant during a single rate determination the isomerization can be expressed by the following equation.

$$\underset{A}{\underset{\sim}{15a}} \underset{}{\overset{HMPT}{\rightleftharpoons}} \underset{B}{\underset{\sim}{15b}}$$

The rate expression for this equilibrium is given by the equation

$$-dA/dt = k_{obs}\,[SiCl]^{x}$$

The following equation may be derived[32] from the preceeding rate equation.

$$\ln\left[\frac{(A_o - A_e)}{(A - A_e)}\right] = k_{obs}\,t = (k_f + k_r)\,t$$

In this equation A_o equals the initial concentration of 15a, A_e is the concentration at equilibrium, A is the concentration at time t, and k_f and k_r are the rate constants of the forward and reverse reactions. The observed rate constant, k_{obs}, can, therefore, be obtained from the slope of a graph of $\ln[(A_o - A_e)/(A - A_e)]$ versus t. Plots of this type gave straight lines indicating that the isomerization was, indeed, first order in chlorosilane as had been originally assumed. Since this is an equilibrium, $k_{obs} = k_f + k_r$ and $k_f A_e = k_r B_e$, thus the forward rate constant, k_f, can be calculated from the equation $k_{obs} = k_f(1 + A_e/B_e)$.

The order in HMPT was obtained by measuring the rate of isomerization of 15a at several different HMPT concentrations. Due to the manner in which k_{obs} was obtained, k_f can be expressed by the following equation.

$$k_f = k_{1+x}[HMPT]^{x}$$

A plot of log k_f versus [HMPT] will, therefore, have a slope equal to x.

Since an order of 1.5 was obtained from the preceeding graph (Figure A-7), k_f could include a first and second order term giving the following equation.

$$k_f = k_2[HMPT] + k_3[HMPT]^2$$

A graph of $k_f/[HMPT]$ versus [HMPT] should give a straight line if the preceeding equation is correct for this isomerization. When this graph was plotted (Figure A-8), a straight line resulted, and the values of k_2 (0.0143 $M^{-1}sec^{-1}$) and k_3 (28.81 $M^{-2}sec^{-1}$) were obtained from the intercept and slope of the line.

The activation parameters were obtained in the usual manner from the equation, $k = A \exp(-E_a/RT)$, by plotting ln k_f versus 1/T (Figure A-17). The slope of the line is equal to the value $-E_a/R$. The value ΔH^* can be calculated from the equation $\Delta H^* = E_a - RT$, and ΔS^* can be calculated from the value for the intercept. The values of k_f used in the plot were obtained by measuring the rate of isomerization of a solution containing 0.5 ml of 1 x 10^{-2}M HMPT in CCl_4 and 0.5 ml of 1.81M silyl chloride in CCl_4 at various temperatures. See Appendix for the actual data and graphs obtained in the preceeding study.

Isomerization of cis-1-chloro-1,2-dimethylsilacyclopentane

1. DMSO-d_6- cis-1-Chloro-1,2-dimethylsilacyclopentane (0.5 ml of a 1.72M solution in CCl_4) and DMSO-d_6 (0.03 g) were placed in an NMR tube. The solution turned cloudy and a strong odor was noticeable immediately after addition. An NMR taken within 10 min of mixing showed complete isomerization (i.e. a Z:E ratio of 53.8:46.2).

2. Sulfolane- cis-1-Chloro-1,2-dimethylsilacyclopentane (0.5 ml of a 0.85M solution in CCl_4) and 0.05 g sulfolane were placed in an NMR tube. NMR spectra showed slight isomerization after 2 hr and complete isomerization after 2 days.

3. n-Bu_4NF- cis-1-Chloro-1,2-dimethylsilacyclopentane (0.076g, 0.0005M)

and 0.28 ml of a 0.1M solution of n-Bu_4NF in $CDCl_3$ were placed in an NMR tube. An NMR taken immediately after mixing showed one peak in the Si-Me region. The peak was located between the cis-and trans-silyl chloride bands.

4. n-Pr_4NCl- cis-1-Chloro-1,2-dimethylsilacyclopentane (0.082g, 0.00055 M) and n-Pr_4NCl (0.0106g, 0.00005M) were dissolved in 0.5 ml $CDCl_3$. An NMR taken immediately after mixing showed one peak in the Si-Me region. The peak was located between those for the cis-and trans-silyl chloride Si-Me peaks.

5. Pyridine- Equivalent amounts of cis-1-chloro-1,2-dimethylsilacyclopentane and pyridine were dissolved in CCl_4 and placed in an NMR tube. A white fluffy solid was observed immediately after mixing. An NMR spectrum showed that the chlorosilane had completely isomerized.

6. THF- Approximately equal amounts of cis-1-chloro-1,2-dimethylsilacyclopentane and THF were placed in an NMR tube and heated at 60°C. An NMR spectrum showed complete isomerization after about 8 hours.

7. CCl_4- No isomerization was apparent for a 1.81M solution of cis-1-chloro-1,2-dimethylsilacyclopentane in CCl_4 after approximately 3 months.

Halide Exchange

1. 1-Chloro-1,2-dimethylsilacyclobutane (0.0928 g, 0.0007M), 1,2-dimethylsilacyclopentane (0.102 g, 0.0007M), and n-Bu_4NF (0.002 g, 7 x 10^{-6}M) were dissolved in $CDCl_3$. An NMR spectrum showed no apparent change after 2 days. 1-Chloro-1,2-dimethylsilacyclobutane (0.06 g, 4.4 x 10^{-4}M), 1,2-dimethyl-1-fluorosilacyclopentane (0.1g, 7.9 x 10^{-4}M), and n-Bu_4NF (0.614g, 2.3 x 10^{-4}M) were dissolved in 0.5 ml $CDCl_3$. An

NMR spectrum showed slow formation of 1-fluoro-1,2-dimethylsilacyclobutane and 1-chloro-1,2-dimethylsilacyclopentane.

2. 1-Bromo-1,2-dimethylsilacyclobutane (0.085g, 0.0005M) and 1-chloro-1,2-dimethylsilacyclopentane (0.093g, 0.0006M) were dissolved in 0.5 ml $CDCl_3$. After 5 days, a small amount of 1-chloro-1,2-dimethylsilacyclopentane and 1-bromo-1,2-dimethylsilacyclobutane had formed.

3. 1-Bromo-1,2-dimethylsilacyclobutane (0.1g, 0.0006M) and 1-chloro-1,2-dimethylsilacyclopentane (0.08g, 0.0005M) were dissolved in 0.5 ml of a 1 x 10^{-2}M HMPT in CCl_4 solution. An NMR taken immediately after mixing showed formation of 1-chloro-1,2-dimethylsilacyclobutane and 1-bromo-1,2-dimethylsilacyclopentane.

4. 1-Bromo-1,2-dimethylsilacyclobutane (0.07g, 0.0004M) and 1-chloro-1,2-dimethylsilacyclopentane (0.09g, 0.0006M) were dissolved in 0.5 ml CCl_4. After 5 days, no isomerization could be observed by NMR.

5. 1-Bromo-1,2-dimethylsilacyclobutane, 1-chloro-1,2-dimethylsilacyclopentane, and n-Bu_4NF were mixed in a molar ratio of 350:330:1. The mixture was dissolved in $CDCl_3$. An NMR spectrum immediately after mixing showed the formation of 1-chloro-1,2-dimethylsilacyclobutane and 1-bromo-1,2-dimethylsilacyclopentane.

Isomerization of 1,2-dimethyl-1-fluorosilacyclopentane

1. HMPT- cis-1,2-Dimethyl-1-fluorosilacyclopentane (0.5 ml of a 0.7M solution in CCl_4) and 0.5 ml of a 1 x 10^{-3}M HMPT solution were placed in an NMR tube. No apparent isomerization was observed by NMR after 4 days. HMPT and trans-1,2-dimethyl-1-fluorosilacyclopentane were mixed in a molar ratio of 3:7 and dissolved in CCl_4. The isomerization was followed by NMR by comparing the heights of the Si-Me peaks.

Time(days)	Ratio (cis/trans)
0	1/6
1	1/4.5
2	1/3
3	1/1.8
4	1/1.5
5	5.5/4.5

2. DMSO- cis-1,2-Dimethylsilacyclopentane (0.5 ml of a 0.7M solution in CCl_4) and DMSO-d_6 (0.087g) were placed in an NMR tube. No apparent isomerization was noted by NMR after 4 days.

3. n-Bu_4NF- cis-1,2-Dimethyl-1-fluorosilacyclopentane (0.063g, 0.0005M) and 0.3 ml of a 0.1M solution of n-Bu_4NF in $CDCl_3$ were placed in an NMR tube. An NMR spectrum showed that the fluorosilane began to isomerize after 15 minutes, but isomerization was not complete after one day.

4. n-Pr_4NCl- cis-1,2-Dimethyl-1-fluorosilacyclopentane (0.093g, 0.0007 M) and n-Pr_4NCl (0.0098g, 4.4×10^{-5}M) were dissolved in 0.5 ml $CDCl_3$. No apparent isomerization was visible by NMR after 5 days. Large quantities of the salt gave slow isomerization.

5. 1,2-Dimethyl-1-fluorosilacyclopentane was dissolved in CH_3OD. An NMR spectrum showed immediate isomerization.

6. DMF- Equivalent molar quantities of DMF and trans-1,2-dimethyl-1-fluorosilacyclopentane were dissolved in CCl_4. The isomerization was followed by NMR using a comparison of the cis- and trans- Si-Me peak heights.

Time(hours)	Ratio(cis/trans)
0	1/6.5
2	1/2.8
48	1/2.6

7. DMSO-d_6- 1,2-Dimethyl-1-fluorosilacyclopentane and DMSO-d_6 were mixed in a 1:2 ratio and dissolved in CCl_4. The isomerization was followed as before.

Time(hours)	Ratio(cis/trans)
0	1/10.5
2	1/10.5
24	1/10.5
72	1/8.5

8. Methanol- 1,2-Dimethyl-1-fluorosilacyclopentane and methanol were mixed in a molar ratio of 3:1 and dissolved in CCl_4. The isomerization was followed in the usual manner.

Time(hours)	Ratio(cis/trans)
0	1/4.5
2	1/4.1
24	1/3.5
72	1/2.8

Isomerization of SiH by n-Bu_4NF in $CDCl_3$

A 91:9 mixture of cis- hydride and trans- hydride (0.16g, 1.2×10^{-3}M), n-Bu_4NF (0.02645g, 1×10^{-4}M), and 0.8 ml $CDCl_3$ were placed in a reaction vial. An NMR spectrum of the mixture was taken 6 days later.

No isomerization was detected.

Isomerization of 1,2-dimethylsilacyclopentane by Cyanide ion

A solution of cyanide ion in DMF was prepared by shaking excess KCN with a 95% DMF/H_2O solution and then allowing the solution to stand over excess KCN for several days. Benzene (5 microliters, internal standard) and 25 microliters trans-1,2-dimethylsilacyclopentane were added to 0.5 ml of the DMF/KCN solution. The reaction was followed by GLPC (3' x 1/8" column of 10% QF-1 joined to a 16' x 1/8" column of 15% Apiezon L; 120°C, isothermal).

Time(min)	Hydride	
	%cis	%trans
15	100	0
30	100	0
190	100	0
1725	72	28

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APPENDIX

The Kinetics of the Isomerization of E-1-Chloro-1,2-dimethylsilacyclopentane

Table A-1. Isomerization of E-1-Chloro-1,2-dimethylsilacyclopentane[a] (15a) by 1 x 10^{-4}M HMPT in CCl_4 at 45°C. [Run 1].

Time(hr)	Relative Area[b]		Time(hr)	Relative Area[b]	
	15a	15b		15a	15b
3.58	19	146	26.78	39	158
	18	151		38	153
	18	152		37	151
6.00	20	160	29.37	35	149
	21	157		35	149
	19	156		34	152
9.68	22	161	32.12	43	148
	20	152		40	150
	20	155		40	150
11.25	21	149	46.32	50	142
	20	150		49	134
	22	150		50	136
21.10	34	148	52.83	49	139
	33	152		49	139
	34	147		50	137

[a] 0.5M in CCl_4

[b] From NMR

Table A-2. Isomerization of E-1-Chloro-1,2-dimethylsilacyclopentane[a] by 1 x 10^{-4}M HMPT in CCl_4 at 45°C. [Run 2].

Time(hr)	Relative Area[b]		Time(hr)	Relative Area[b]	
	15a	15b		15a	15b
3.65	19	149	26.83	37	151
	18	150		36	153
	18	144		36	153
5.95	18	165		33	155
	20	153	29.42	37	154
	19	160		39	149
9.67	18	147		39	150
	21	141	32.15	46	152
	20	157		44	152
	20	148		45	158
11.30	22	156		43	153
	22	150	46.25	51	135
	22	154		54	142
21.33	31	165		52	136
	32	187	52.75	59	132
	32	170		53	134
	32	175		55	134

[a] 0.9M in CCl_4

[b] From NMR

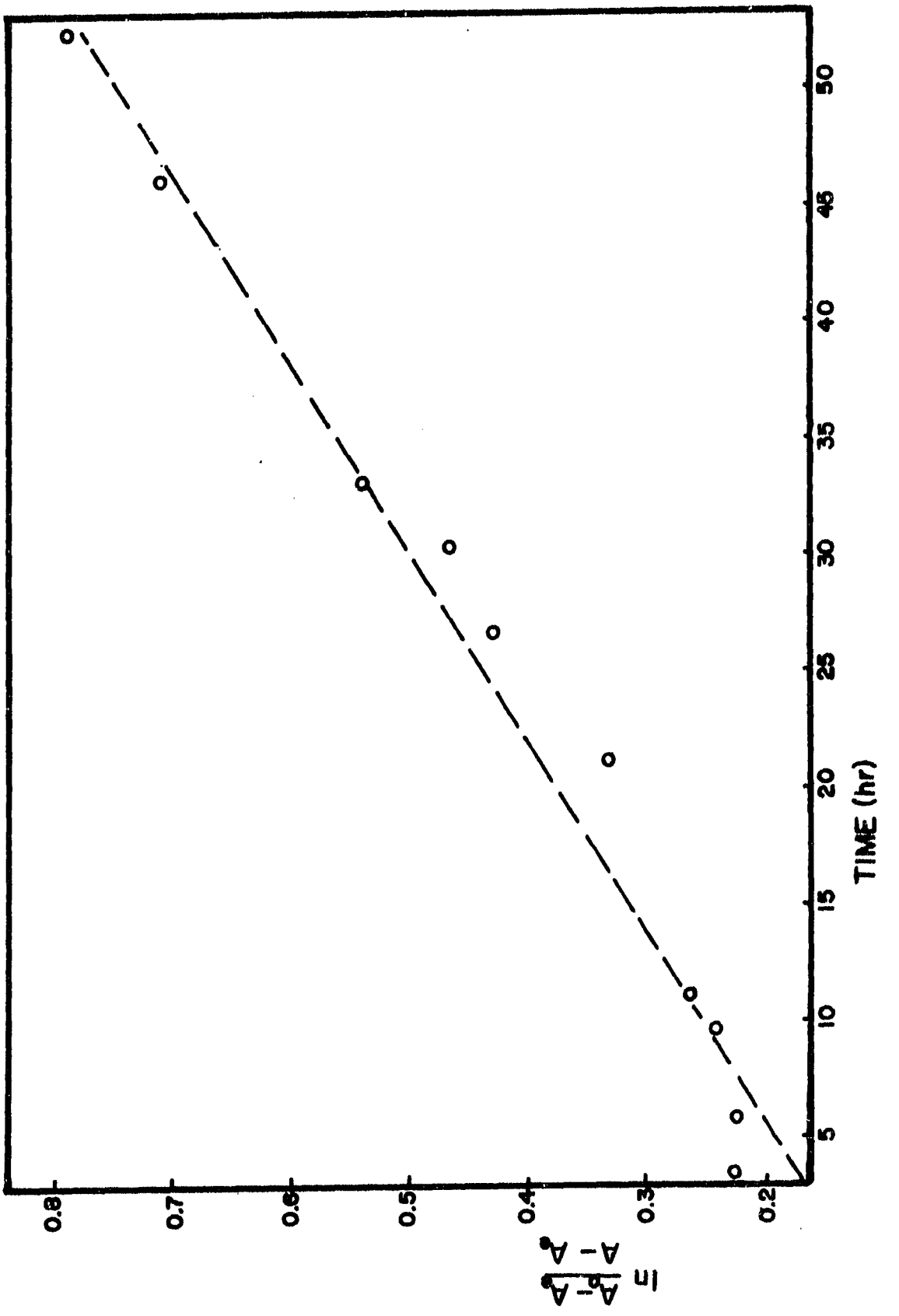

Figure A-1. Graph of $\ln(A_0-A_e)/(A-A_e)$ vs. Time for the Isomerization of E-Chloro-1,2-dimethylsilacyclopentane by 1×10^{-4} M HMPT in CCl_4 at 45° (Run 2)

Table A-3. Isomerization of E-1-Chloro-1,2-dimethylsilacyclopentane[a] (15a) by 2.5×10^{-4} HMPT in CCl_4 at 45°C.

Time(hr)	Relative Area[b]		Time(hr)	Relative Area[b]	
	15a	15b		15a	15b
3.73	21	139	11.38	38	119
	22	136		36	117
	21	141		34	123
6.85	27	138	21.15	60	117
	30	142		61	121
	24	141		60	119
	24	149	26.73	69	117
8.73	33	135		70	112
	33	130		67	115
	33	137	29.30	74	113
	33	132		75	114
9.82	36	127		76	116
	35	128			
	36	131			

[a] 0.9M in CCl_4

[b] From NMR

Figure A-2. Graph of $\ln(A_o-A_e)/(A-A_e)$ vs. time for the Isomerization of E-1-Chloro-1,2-dimethylsilacyclopentane by 2.5×10^{-5} M HMPT in CCl_4 at 45°.

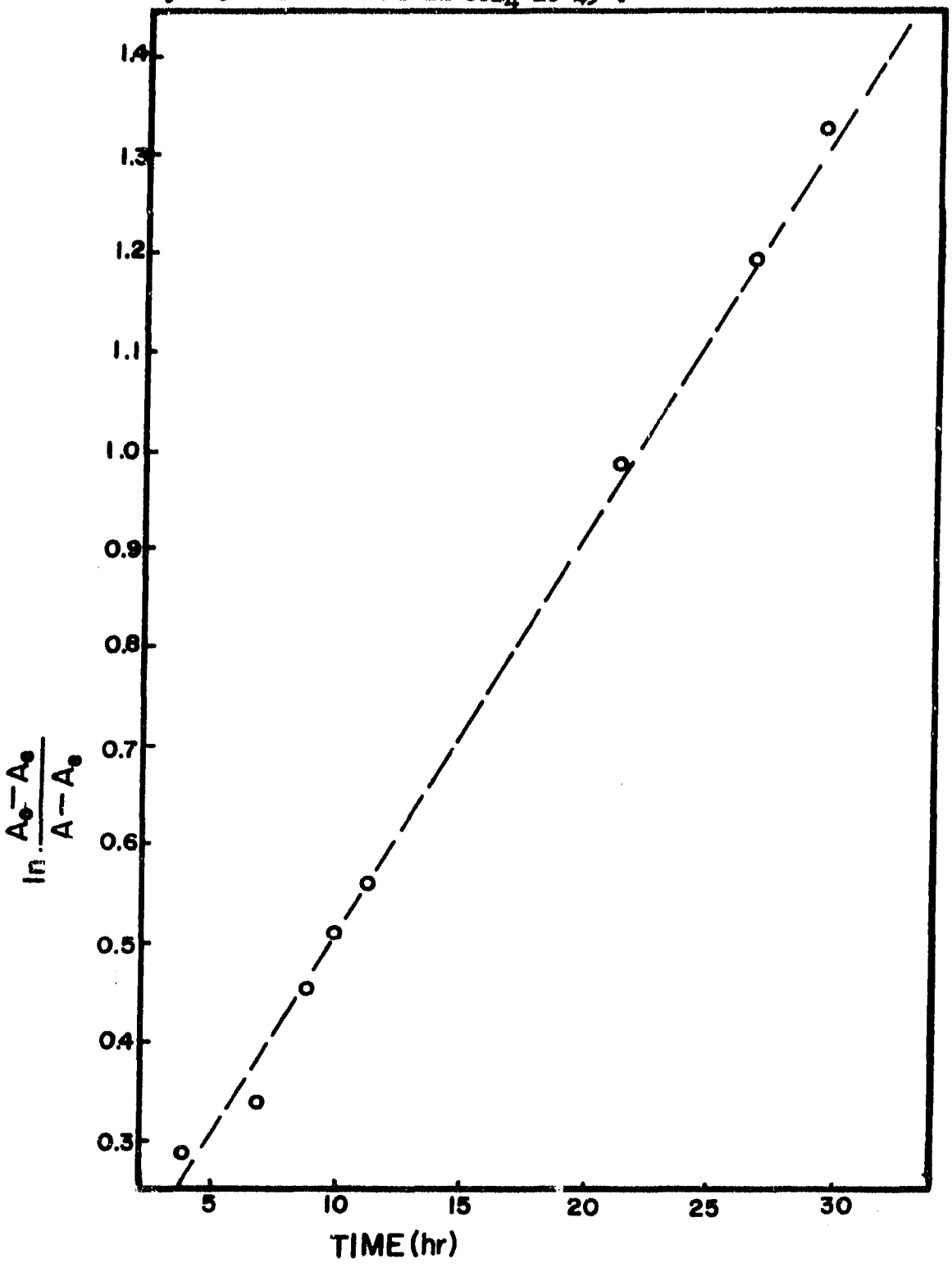

Table A-4. The Isomerization of E-1-Chloro-1,2-dimethylsilacyclopentane[a] (15a) by 5 x 10^{-4}M HMPT in CCl_4 at 45°C. [Run 1].

Time(sec)	Relative Area[b]		Time(sec)	Relative Area[b]	
	15a	15b		15a	15b
800	23	202	6000	44	182
1210	24	194	6400	44	179
1700	27	195	6700	46	172
1800	26	198	7000	47	180
2200	27	194	7300	45	180
2500	28	194	7600	49	180
2900	32	180	8000	47	176
3200	32	179	8400	50	175
3600	32	189	8707	49	180
3910	36	179	9500	52	167
4200	39	186	9700	57	170
4600	41	189	9950	53	171
4900	39	193	10200	53	163
5200	39	186	10500	58	172
5300	43	175	10800	58	167
5700	43	184	11000	60	165

[a] 0.9M in CCl_4

[b] From NMR

Table A-5. Isomerization of E-Chloro-1,2-dimethylsilacyclopentane[a] (15a) by 5 x 10^{-4}M HMPT in CCl_4 at 45°C. [Runs 2 and 3].

Run 2			Run 3		
Time(hr)	Relative Area[b]		Time(hr)	Relative Area[b]	
	15a	15b		15a	15b
3.55	27	117	1.08	27	182
	30	124		29	198
	36	160		28	184
	36	155		27	186
6.82	54	141	3.28	33	142
	49	148		35	136
	53	147		32	141
9.00	51	111	5.83	47	125
	51	111		48	127
	48	111		48	127
9.83	53	109	7.00	51	127
	55	103		52	127
	54	108		51	124
11.53	67	123	7.90	54	127
	68	116		53	125
	67	119		53	124
			9.78	67	117
				66	114
				65	115
				65	111
			11.50	71	109
				74	108
				75	107

[a]0.9M in CCl_4
[b]From NMR

Figure A-3. Graph of $\ln(A_o-A_e)/(A-A_e)$ vs. time for the Isomerization of E-1-Chloro-1,2-dimethylsilacyclopentane by 5×10^{-4} M HMPT in CCl_4 at 45° (Run 2).

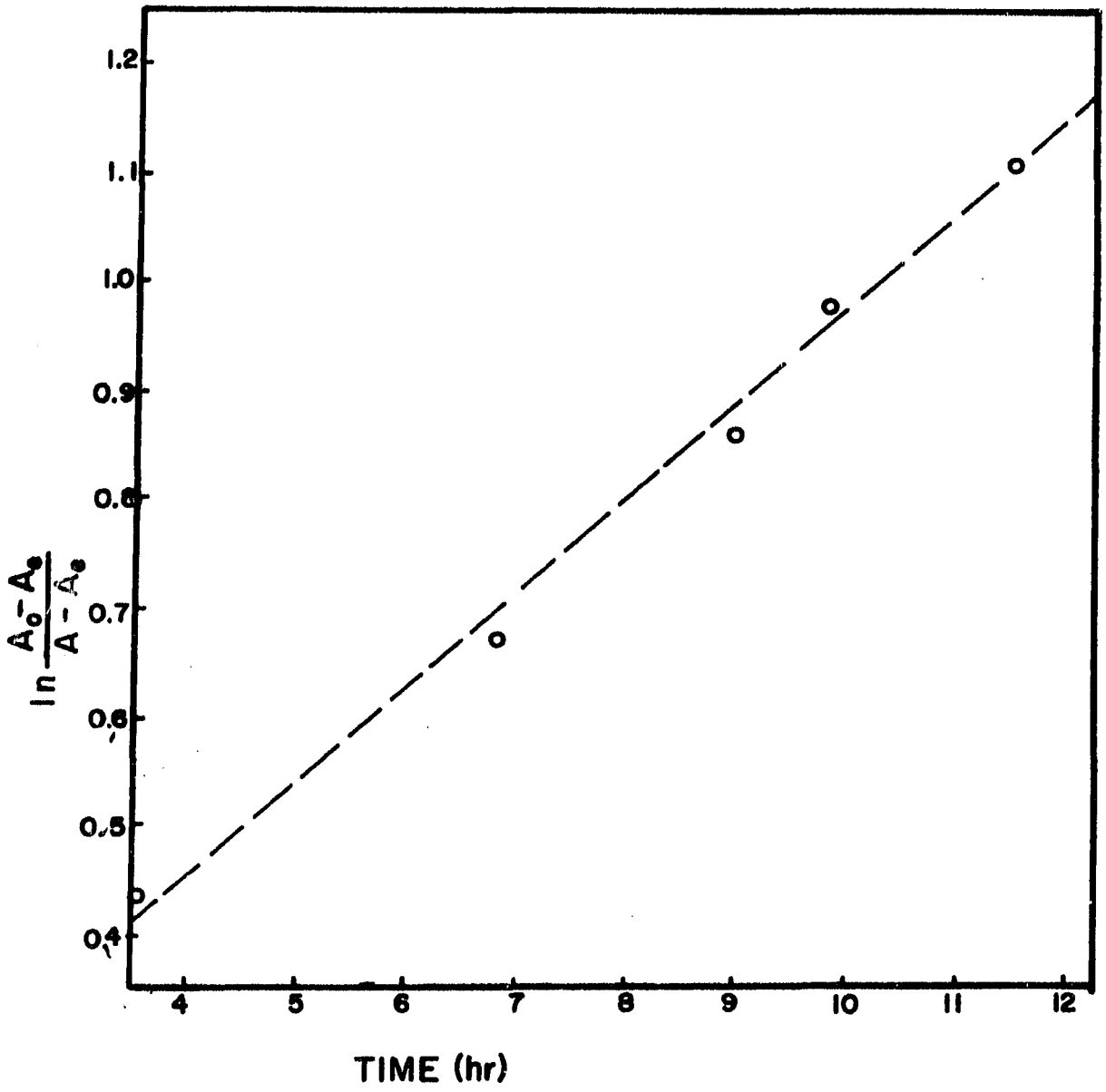

Table A-6. The Isomerization of E-1-Chloro-1,2-dimethylsilacyclopentane[a] (15a) by 2 x 10^{-3}M HMPT in CCl_4 at 45°C. [Run 1].

Time(sec)	Relative Area[b]		Time(sec)	Relative Area[b]	
	15a	15b		15a	15b
390	20	165	1900	41	131
440	22	146	1960	42	136
500	22	145	2000	43	128
560	25	143	2120	46	129
600	28	140	2200	45	133
650	25	159	2310	47	130
750	25	144	2450	48	124
810	30	138	2500	48	127
851	29	152	2600	49	129
900	30	144	2700	51	132
960	31	130	2800	51	116
1000	30	142	2900	51	115
1100	32	151	3040	55	126
1150	32	142	3150	57	119
1210	34	147	3250	54	120
1250	33	133	3310	58	120
1300	34	139	3400	61	116
1350	36	145	3500	60	117
1420	37	147	3605	64	116
1450	35	138	3700	62	116
1500	37	132	3800	62	121
1550	39	135	3905	59	116
1600	40	133	4050	64	118
1700	40	138	4100	63	116
1800	43	137	4200	62	114
1850	43	133	4300	64	113

[a] 0.9M in CCl_4

[b] From NMR

Table A-7. The Isomerization of E-1-Chloro-1,2-dimethylsilacyclopentane[a] (15a) by 2 x 10^{-3}M HMPT in CCl_4 at 45°C. [Run 2].

Time(sec)	Relative Area[b]		Time(sec)	Relative Area[b]	
	15a	15b		15a	15b
200	17	114	2150	65	149
300	24	172	2200	62	140
400	28	182	2300	62	146
505	30	179	2400	66	144
600	30	178	2500	70	144
800	36	174	2700	72	139
900	39	174	2805	71	145
1000	41	165	2900	73	144
1100	44	165	3000	72	140
1250	46	172	3100	72	132
1300	46	168	3200	73	130
1400	49	158	3305	75	135
1505	49	168	3400	78	132
1620	52	157	3510	76	136
1750	56	155	3600	78	136
1800	57	153	3700	79	131
1900	59	152	3800	80	138
2000	61	152			

[a] 0.9M in CCl_4

[b] From NMR

Table A-8. Isomerization of E-1-Chloro-1,2-dimethylsilacyclopentane[a] (15a) by 2 x 10^{-3}M HMPT in CCl_4 at 45°C. [Run 3].

Time(min)	Relative Area[b]		Time(min)	Relative Area[b]	
	15a	15b		15a	15b
10.5	32	175	26	51	162
12	34	174	28	51	159
13	36	170	29	51	160
14	35	167	30.08	52	160
15	38	162	31	55	164
16	37	164	33	57	158
17	40	158	34	58	154
19	41	164	35	57	156
20	40	156	36	59	152
21	45	161	39	61	154
22	46	160	40	62	158

[a] 0.9M in CCl_4.
[b] From NMR

Table A-9. Isomerization of E-1-Chloro-1,2-dimethylsilacyclopentane[a] (15a) by 2 x 10^{-3}M HMPT in CCl_4 at 45°C. [Run 4].

Time(min)	Relative Area[b]		Time(min)	Relative Area[b]	
	15a	15b		15a	15b
4	21	156	27	45	146
4.5	20	158	27.5	42	143
5	22	154	29	47	140
6	22	152	30.5	47	146
7.5	25	154	32	46	144
9	26	148	33.5	48	135
10	27	155	36	49	134
11.5	30	161	37.5	51	137
13	31	155	39	52	135
14.5	34	152	41	54	129
16	34	157	42	57	133
18	37	146	43.5	55	133
18.5	37	148	45	57	131
20	41	148	46.5	56	136
21.5	39	153	48	57	130
23	40	150	49	57	128
25.5	41	144	50.5	60	132

[a] 0.9M in CCl_4

[b] From NMR

Figure A-4. Graph of $\ln(A_o-A_e)/(A-A_e)$ vs time for the Isomerization of E-1-Chloro-1,2-dimethylsilacyclopentane by 2×10^{-3} M HMPT in CCl_4 at 45° (Run 2).

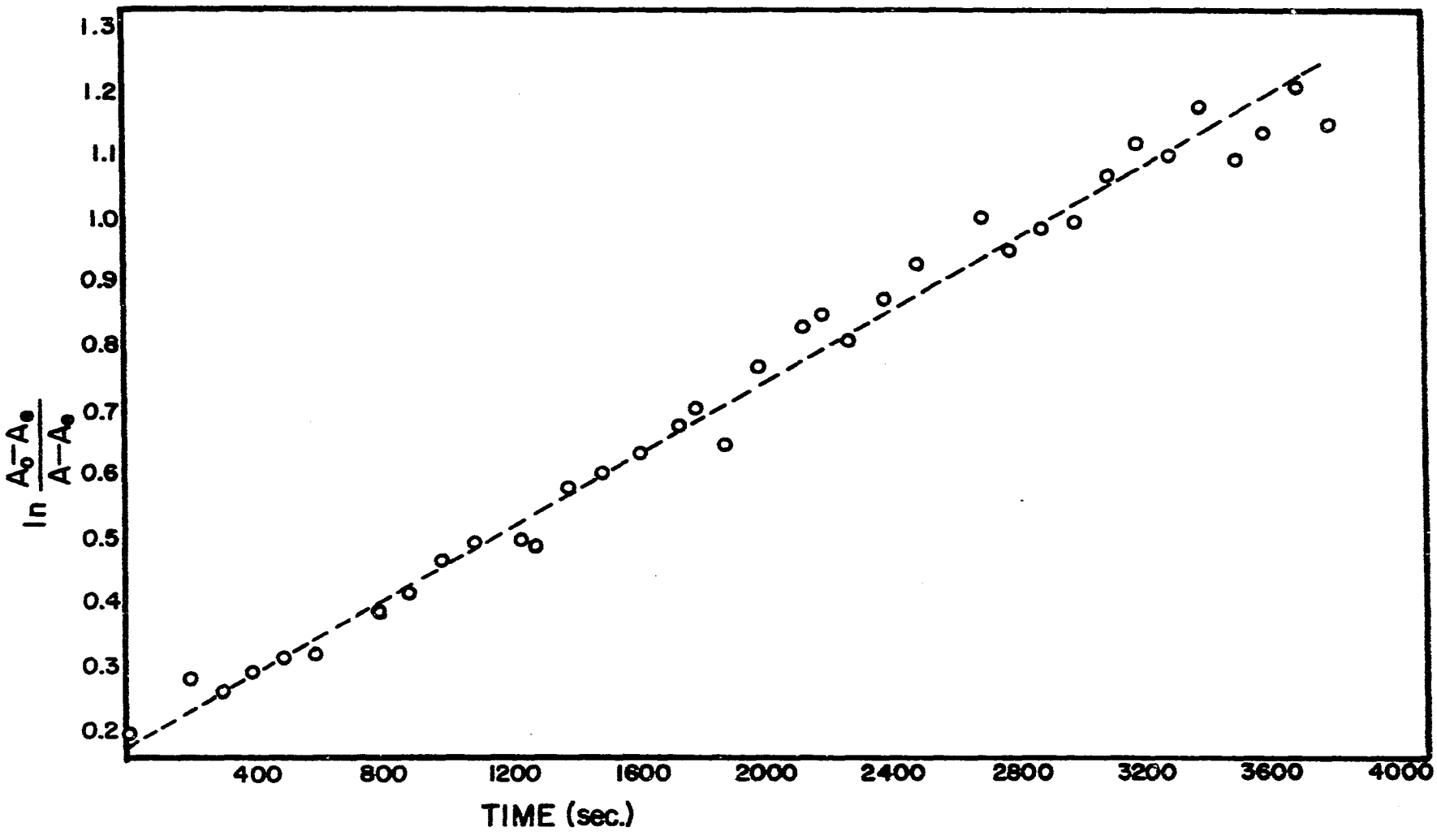

Table A-10. Rate of Isomerization of E-1-Chloro-1,2-dimethylsilacyclopentane[a] (15a) by 3 x 10^{-3}M HMPT in CCl_4 at 45°C. [Run 1].

Time(sec)	Relative Area[b]		Time(sec)	Relative Area[b]	
	15a	15b		15a	15b
180	29	180	1160	67	154
210	29	184	1250	68	152
250	30	175	1300	70	157
380	35	176	1350	74	152
430	40	169	1400	72	154
490	42	164	1500	79	150
540	44	176	1550	76	149
700	48	166	1600	78	154
750	51	164	1700	85	148
800	54	160	1750	85	143
850	55	154	1850	83	141
950	57	158	1900	85	138
1000	61	162	1950	90	146
1050	62	152	2000	86	145

[a] 0.9M in CCl_4

[b] From NMR

Table A-11. The Isomerization of E-1-Chloro-1,2-dimethylsilacyclopentane[a] (15a) by 3 x 10^{-3}M HNPT in CCl_4 at 45°C. [Run 2].

Time(sec)	Relative Area[b]		Time(sec)	Relative Area[b]	
	15a	15b		15a	15b
190	31	181	1150	66	150
250	32	185	1200	64	142
310	36	173	1250	66	147
350	36	173	1300	63	142
400	39	175	1400	71	139
450	42	170	1450	72	142
500	43	160	1500	73	150
550	45	165	1550	74	141
600	47	161	1600	76	133
700	49	158	1650	74	135
760	53	162	1700	80	137
800	54	151	1750	79	138
850	58	160	1800	76	136
900	53	152	1850	81	131
950	58	152	1900	81	139
1000	59	145	1950	80	132
1050	60	150	2000	78	128
1100	62	148			

[a] 0.9M in CCl_4

[b] From NMR

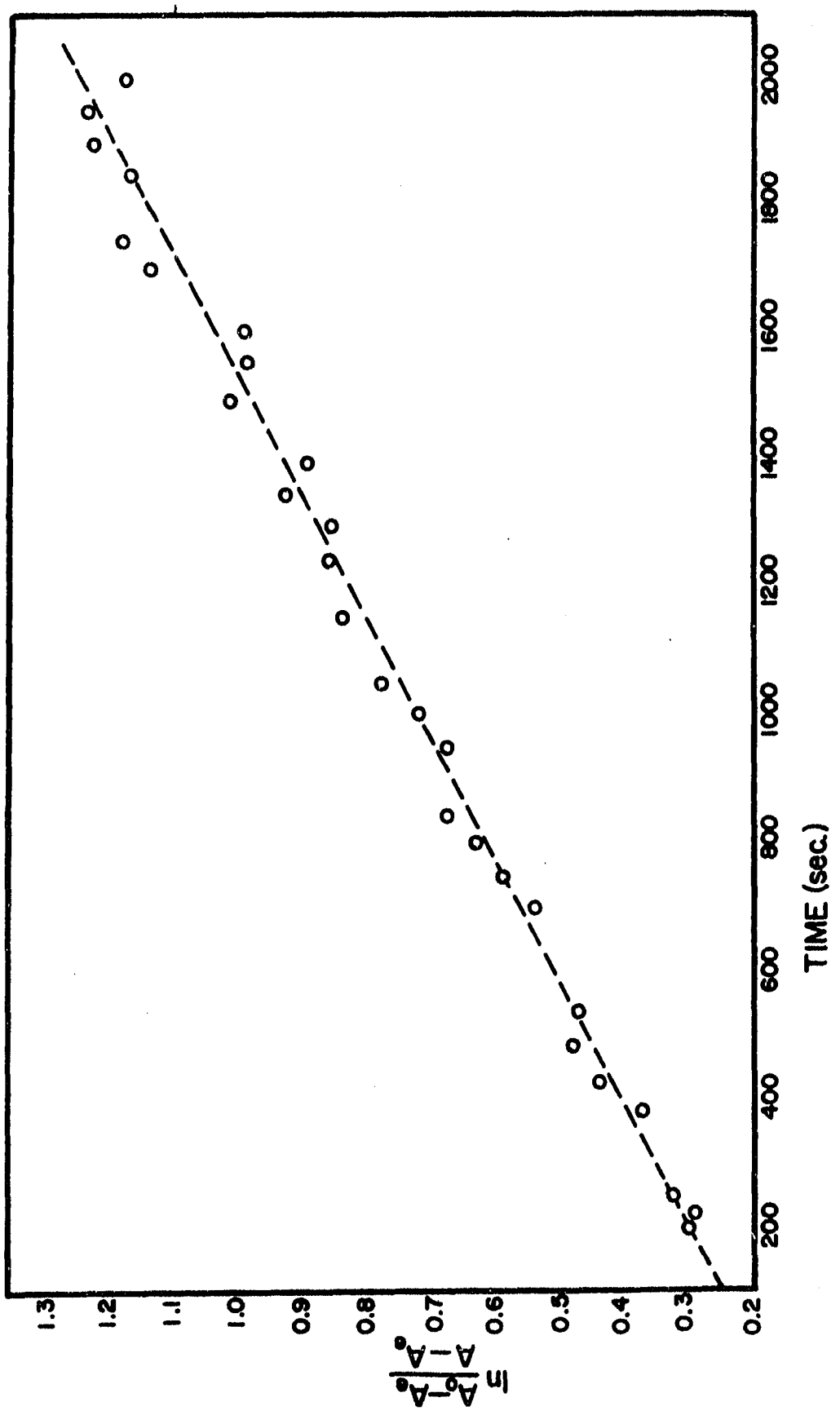

Figure A-5. Graph of $\ln(A_o - A_e)/(A - A_e)$ vs time for the Isomerization of Ξ-1-Chloro-1,2-dimethylsilacyclopentane by 3×10^{-3}M HMPT in CCl_4 at 45°(Run 1).

Table A-12. The Isomerization of E-1-Chloro-1,2-dimethylsilacyclopentane[a] (15a) by 5 x 10^{-3}M HMPT in CCl_4 at 45°C. [Runs 1 and 2].

Run 1			Run 2		
Time(sec)	Relative Area[b]		Time(sec)	Relative Area[b]	
	15a	15b		15a	15b
135	28	136	130	25	124
170	30	135	160	36	151
210	35	133	200	41	153
240	37	131	230	43	140
280	42	123	260	47	146
320	43	121	300	52	138
350	46	127	330	50	142
380	49	120	360	53	135
410	50	113	390	58	133
450	52	109	430	60	133
480	54	112	470	63	131
510	56	112	510	66	127
540	59	110	550	67	126
580	59	110	580	69	127
610	63	106	610	71	120
640	65	105	640	62	115
670	65	108	670	72	123
710	65	106	710	71	115
740	67	101	741	78	118
780	67	99	780	78	115
820	69	97	840	83	115
860	74	100	880	84	116
900	73	100			

[a] 0.9M in CCl_4

[b] From NMR

Figure A-6. Graph of $\ln(A_o-A_e)/(A-A_e)$ vs time for the Isomerization of E-1-Chloro-1,2-dimethylsilacyclopentane by 5×10^{-3}M HMPT in CCl_4 at 45° (Run 1).

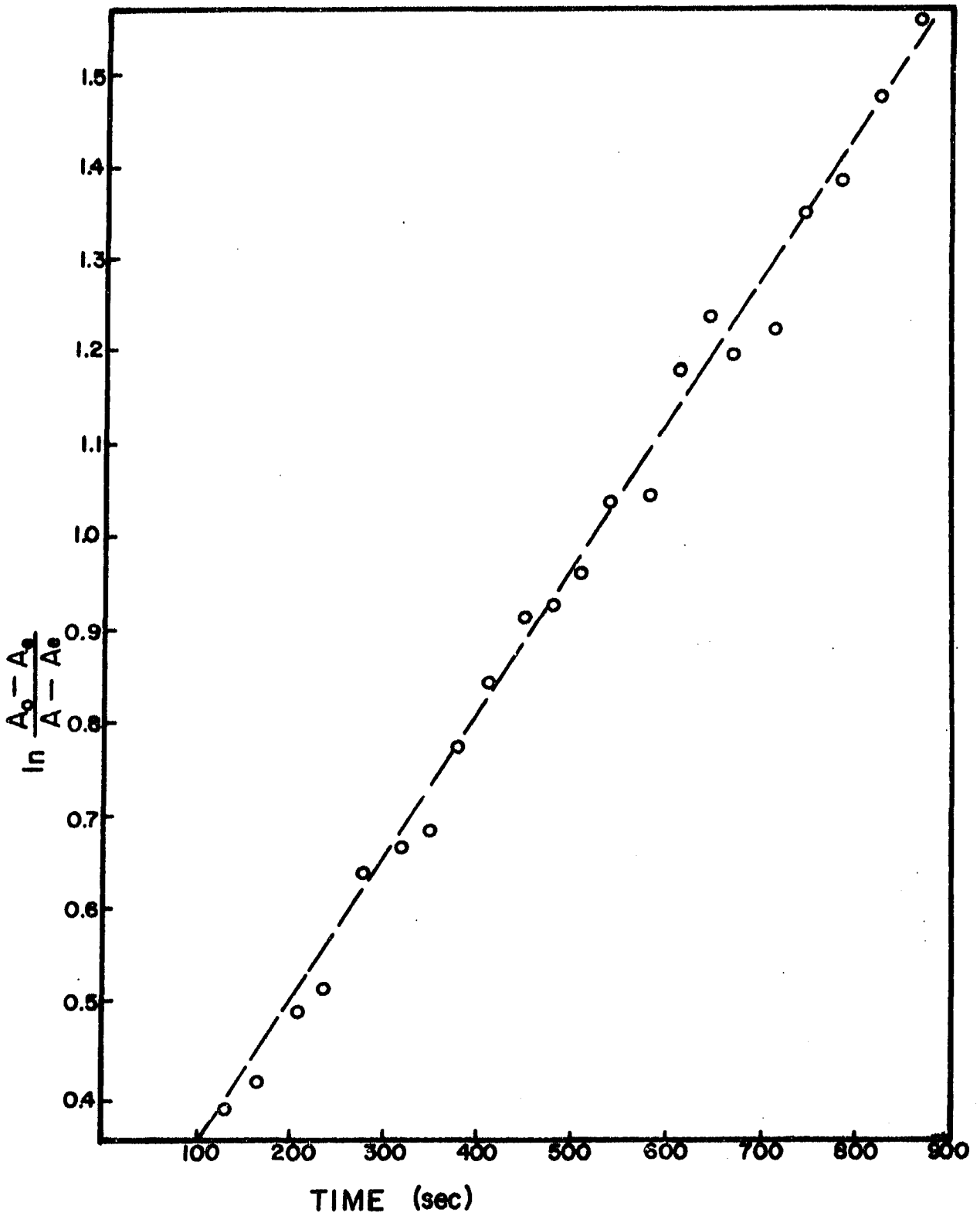

Table A-13. Rate Constants derived from Data in Tables A-1 through A-12.

Table	[HMPT]	$k_{obs} \times 10^6$, sec^{-1}	$k_f^* \times 10^6$, sec^{-1}	r
A-1	1×10^{-4}M(Run 1)	2.8 ± 0.3	1.5 ± 0.2	0.986
A-2	1×10^{-4}M(Run 2)	3.7 ± 0.3	1.8 ± 0.2	0.989
A-3	2.5×10^{-4}M	11.6 ± 0.4	6.2 ± 0.2	0.998
A-4	5×10^{-4}M(Run 1)	43 ± 2	23 ± 1	0.987
A-5	5×10^{-4}M(Run 2)	24 ± 2	13 ± 1	0.996
A-5	5×10^{-4}M(Run 3)	29 ± 4	16 ± 2	0.983
A-6	2×10^{-3}M(Run 1)	222 ± 8	119 ± 4	0.991
A-7	2×10^{-3}M(Run 2)	280 ± 10	149 ± 6	0.992
A-8	2×10^{-3}M(Run 3)	230 ± 10	125 ± 6	0.993
A-9	2×10^{-3}M(Run 4)	227 ± 8	122 ± 5	0.994
A-10	3×10^{-3}M(Run 1)	530 ± 20	290 ± 10	0.995
A-11	3×10^{-3}M(Run 2)	510 ± 30	270 ± 10	0.991
A-12	5×10^{-3}M(Run 1)	1580 ± 60	850 ± 20	0.996
A-12	5×10^{-3}M(Run 2)	1490 ± 70	800 ± 40	0.993

Table A-13a. Dependence of Isomerization of 15a on HMPT as derived from Graph of log k_f versus [HMPT]. Figure A-7.

Slope (dependence on [HMPT])	r
1.6 ± 0.1	0.998

Table A-13b. Values of k_2 and k_3 as derived from Graph of log k_f/[HMPT] vs [HMPT]. Figure A-8.

Slope (k_3, $M^{-2}sec^{-1}$)	Intercept (k_2, $M^{-1}sec^{-1}$)	r
29 ± 1	0.014 ± 0.001	0.994

*k_{eq} = 1.1645

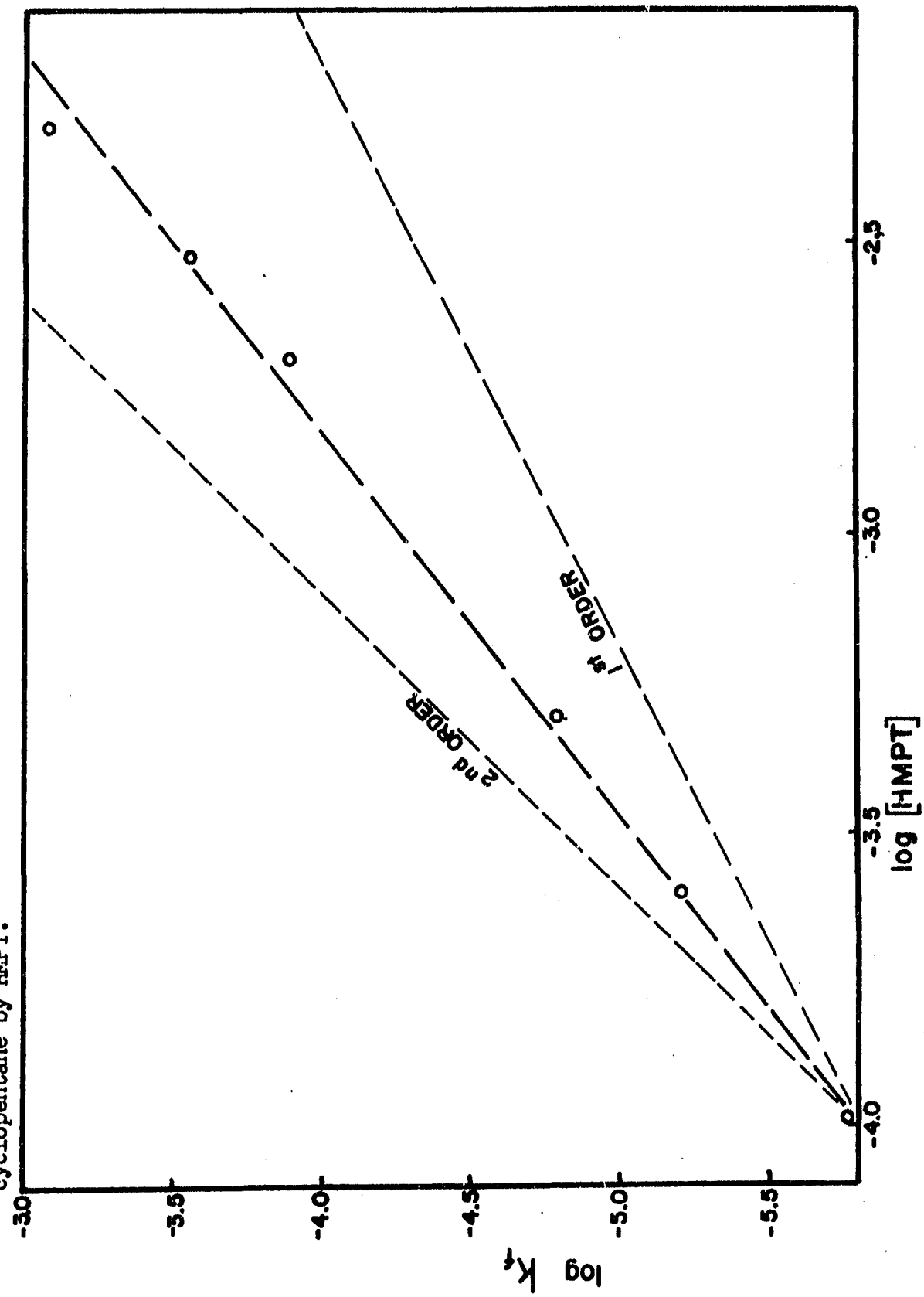

Figure A-7. Graph of log k_f vs [HMPT] for the Isomerization of E-1-Chloro-1,2-dimethylsilacyclopentane by HMPT.

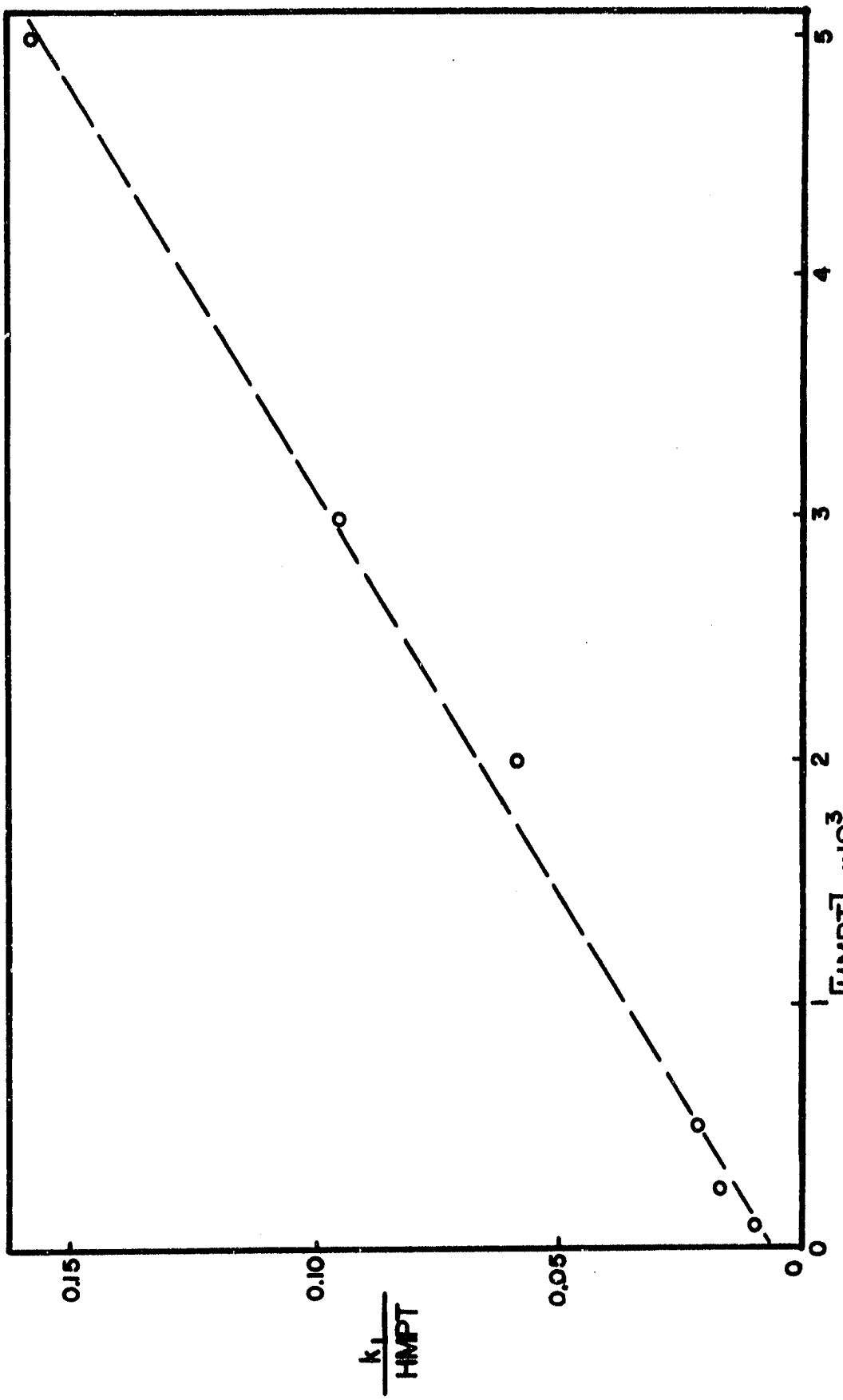

Figure A-8. Graph of log $k_f/[HMPT]$ vs. [HMPT] for the Isomerization of E-1-Chloro-1,2-dimethylsilacyclopentane by HMPT.

Table A-14. Isomerization of E-1-Chloro-1,2-dimethylsilacyclopentane[a] (15a) by 5×10^{-3}M HMPT in CCl_4 at 277°K.

Time(min)	Relative Area[b]		Time(min)	Relative Area[b]	
	15a	15b		15a	15b
3.5	33	160	19	59	129
4	35	156	20	59	131
7	39	148	21	60	132
8	41	144	22	60	131
9	42	143	23	65	127
10	42	142	24	61	126
13	43	142	25	64	131
14	51	142	26	67	135
16	53	137	28	65	124
17	53	131	30	68	126
18	53	133			

[a] 0.9M in CCl_4

[b] From NMR

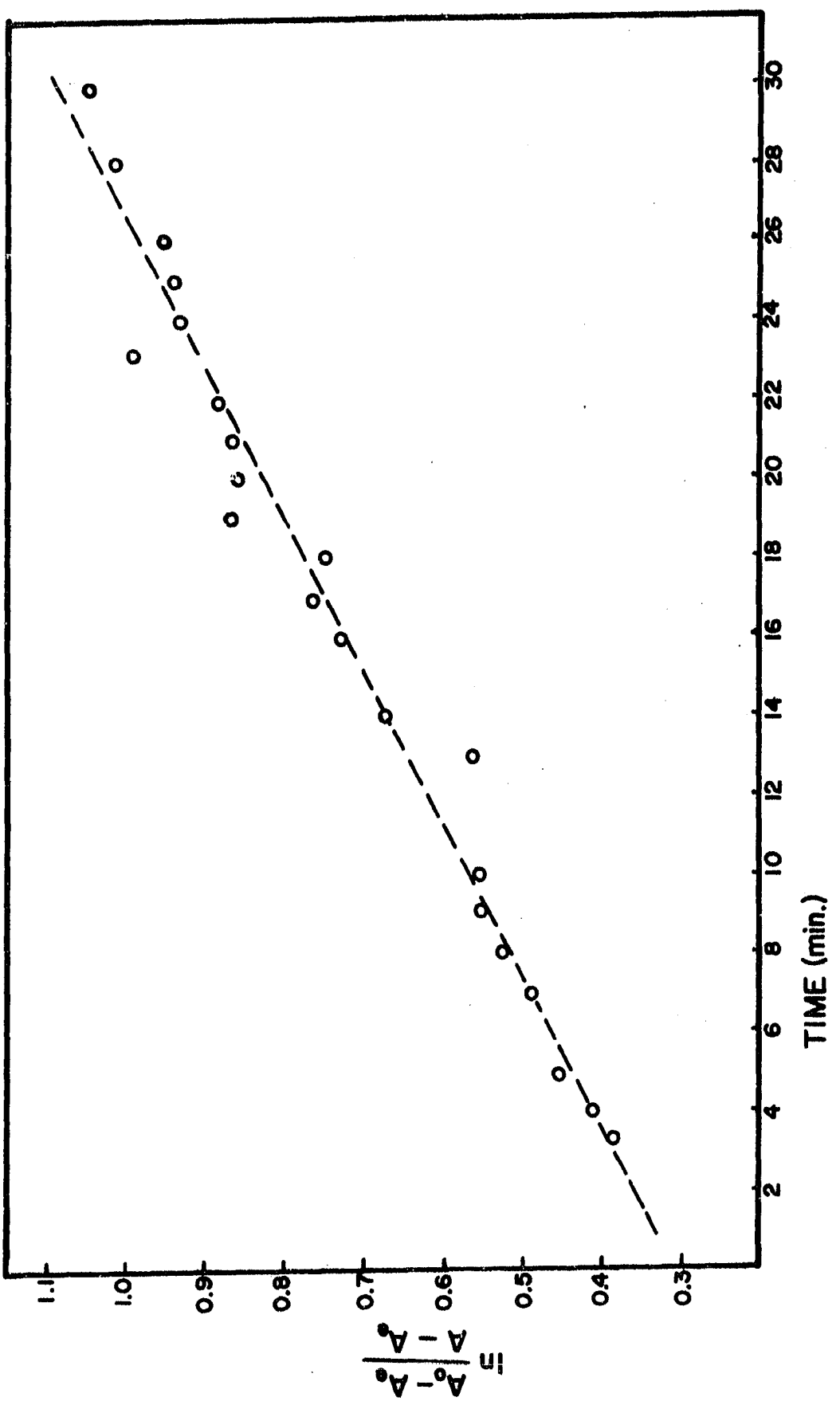

Figure A-9. Graph of $\ln(A_o - A_e)/(A - A_e)$ vs. time for the Isomerization of E-1-Chloro-1,2-dimethylsilacyclopentane by 5×10^{-3} M HMPT in CCl_4 at 277°K.

Table A-15. Isomerization of E-1-Chloro-1,2-dimethylsilacyclopentane[a] (15a) by 5×10^{-3}M HMPT in CCl_4 at 287°K.

Time(min)	Relative Area[b]		Time(min)	Relative Area[b]	
	15a	15b		15a	15b
2	31	168	12	53	143
2.5	31	163	13	54	139
3	32	159	14	61	133
3.67	35	154	16	59	135
5.33	38	149	17	65	135
6	39	152	18	65	133
7	40	152	19	65	131
8	42	149	20	68	128
9	44	143	22	67	129
10	50	141	23	69	126
11	51	140	24	73	125

[a] 0.9M in CCl_4

[b] From NMR

Figure A-10. Graph of $\ln(A_o-A_e)/(A-A_e)$ vs. time for the Isomerization of E-1-Chloro-1,2-dimethylsilacyclopentane by 5×10^{-3}M HMPT in CCl_4 at 287°K.

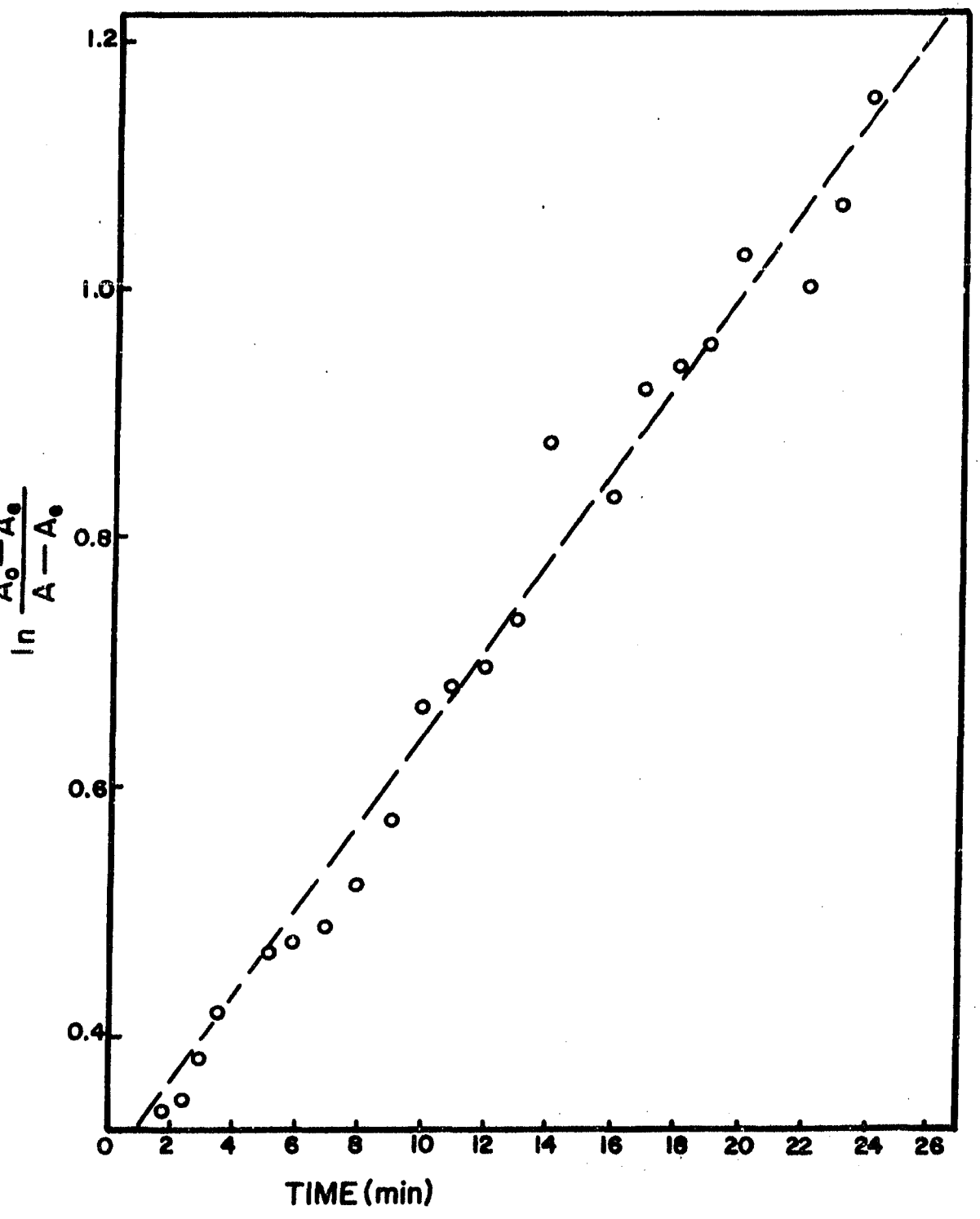

Table A-16. Isomerization of E-1-Chloro-1,2-dimethylsilacyclopentane[a] (15a) by 5 x 10^{-3}M HMPT in CCl_4 at 296°K.

Time(min)	Relative Area[b]		Time(min)	Relative Area[b]	
	15a	15b		15a	15b
2.33	30	135	10.83	57	117
2.83	32	132	11.67	56	112
3.33	33	134	12.50	58	110
4.00	37	134	13.33	60	110
4.67	39	137	14.17	59	110
5.50	42	126	15.00	63	109
6.17	45	126	15.83	67	108
6.83	48	123	16.67	68	109
7.50	49	127	17.50	68	106
8.33	50	118	18.50	67	105
9.17	53	118	19.50	68	101
10.00	54	116	20.50	71	100

[a] 0.9M in CCl_4

[b] from NMR

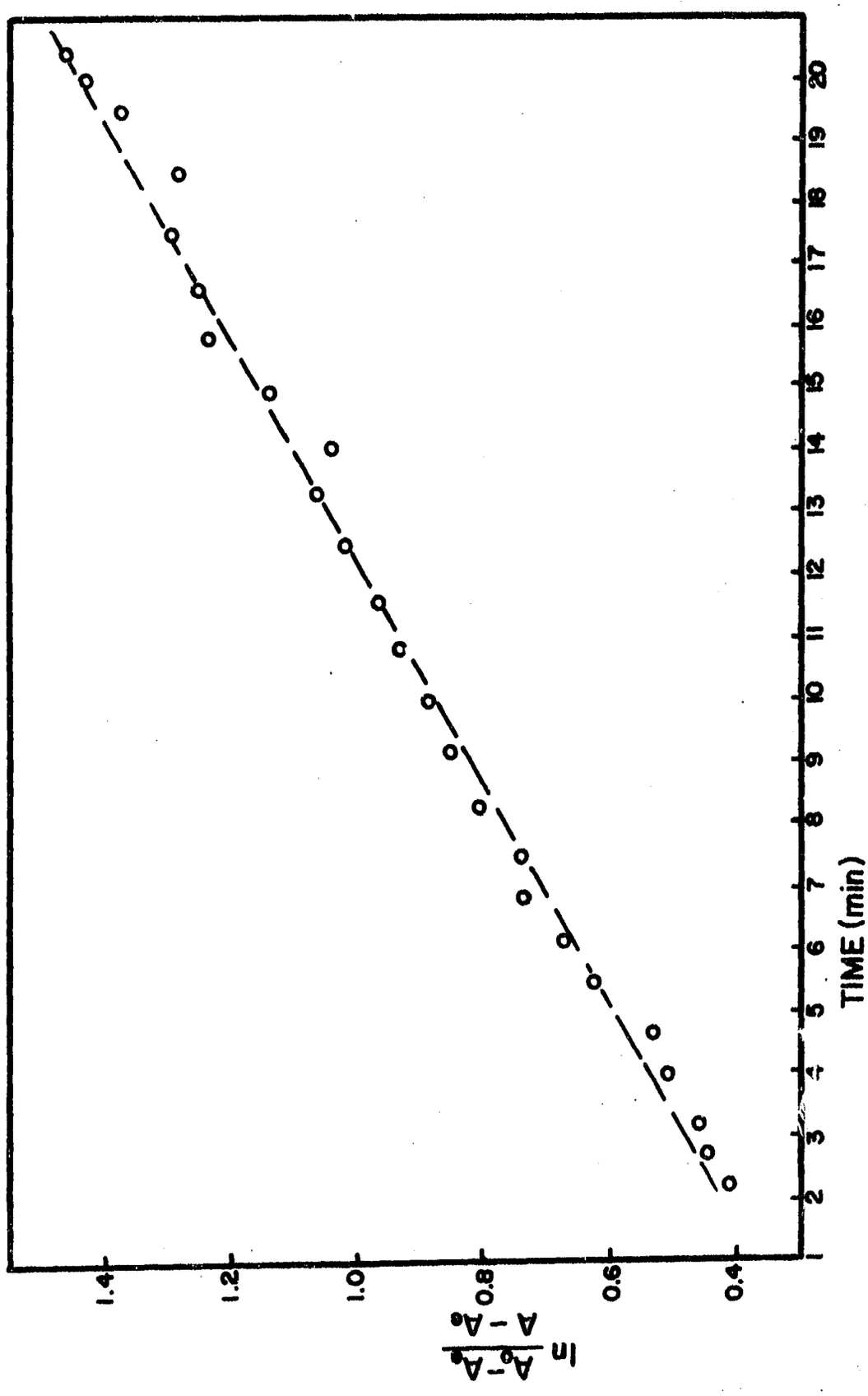

Figure A-11. Graph of $\ln(A_o - A_e)/(A - A_e)$ vs time for the Isomerization of E-1-Chloro-1,2-dimethylsilacyclopentane by 5×10^{-3}M HMPT in CCl_4 at 296°K.

Table A-17. Isomerization of E-1-Chloro-1,2-dimethylsilacyclopentane[a] (15a) by 5 x 10^{-3}M HMPT in CCl_4 at 308°K.

Time(sec)	Relative Area[b]		Time(sec)	Relative Area[b]	
	15a	15b		15a	15b
170	33	144	550	55	105
200	34	147	600	55	118
230	35	139	800	67	114
270	39	137	850	75	112
310	43	135	900	77	113
350	44	128	950	81	112
400	47	132	1000	78	107
450	47	124	1050	84	106
500	52	127			

[a] 0.9M in CCl_4

[b] From NMR

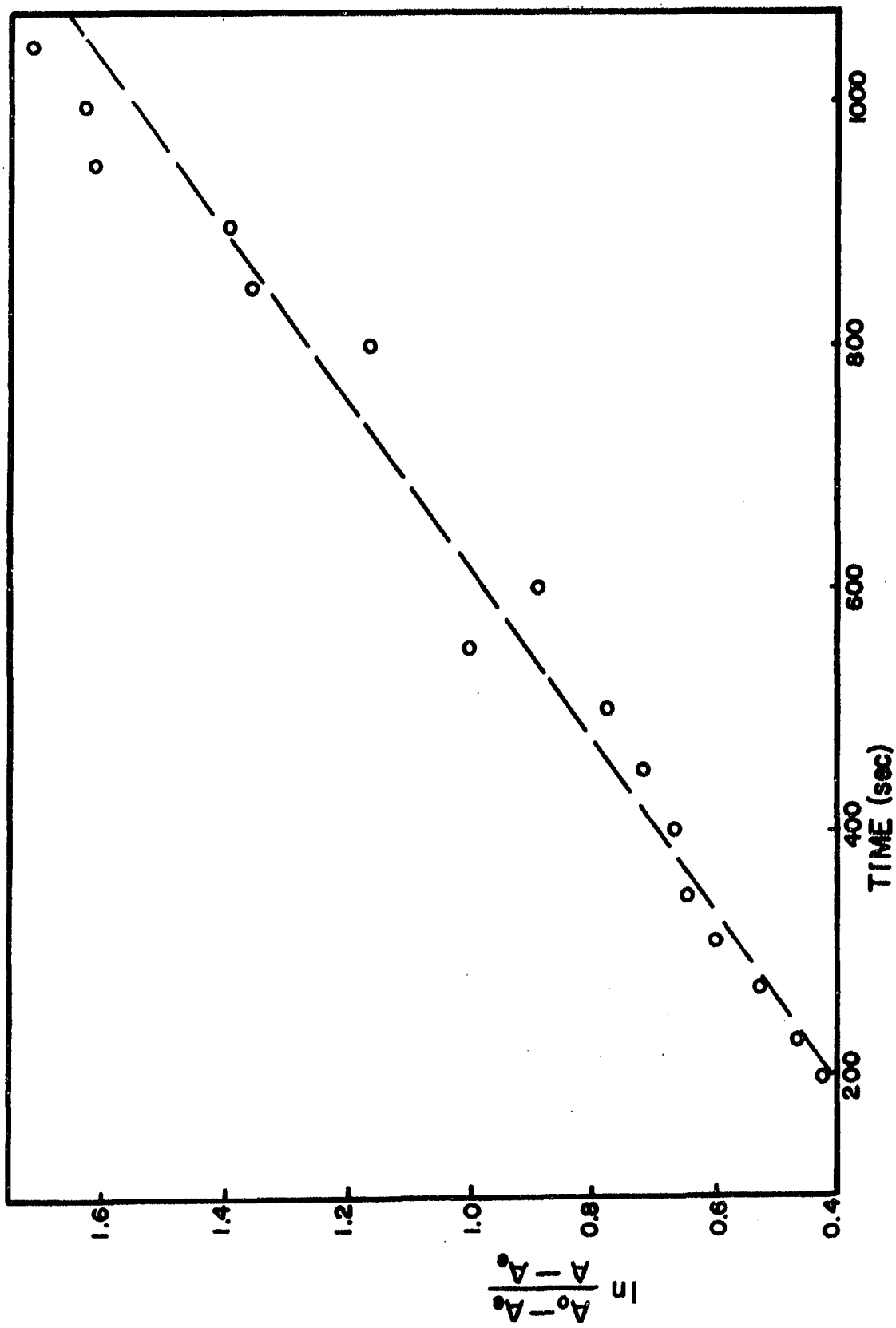

Figure A-12. Graph of $\ln(A_o - A_e)/(A - A_e)$ vs time for the Isomerization of E-1-Chloro-1,2-dimethylsilacyclopentane by 5×10^{-3}M HMPT at 308°K.

Table A-18. Isomerization of E-1-Chloro-1,2-dimethylsilacyclopentane[a] (15a) by 5 x 10^{-3}M HMPT in CCl_4 at 313°K.

Time(sec)	Relative Area[b]		Time(sec)	Relative Area[b]	
	15a	15b		15a	15b
120	35	142	480	53	117
150	37	140	550	59	116
190	40	137	640	68	108
220	43	135	690	70	107
250	45	123	740	70	106
290	49	129	780	73	106
330	49	122	830	76	108
370	53	126	870	77	105
400	55	117	900	78	105
440	57	116			

[a] 0.9M in CCl_4

[b] From NMR

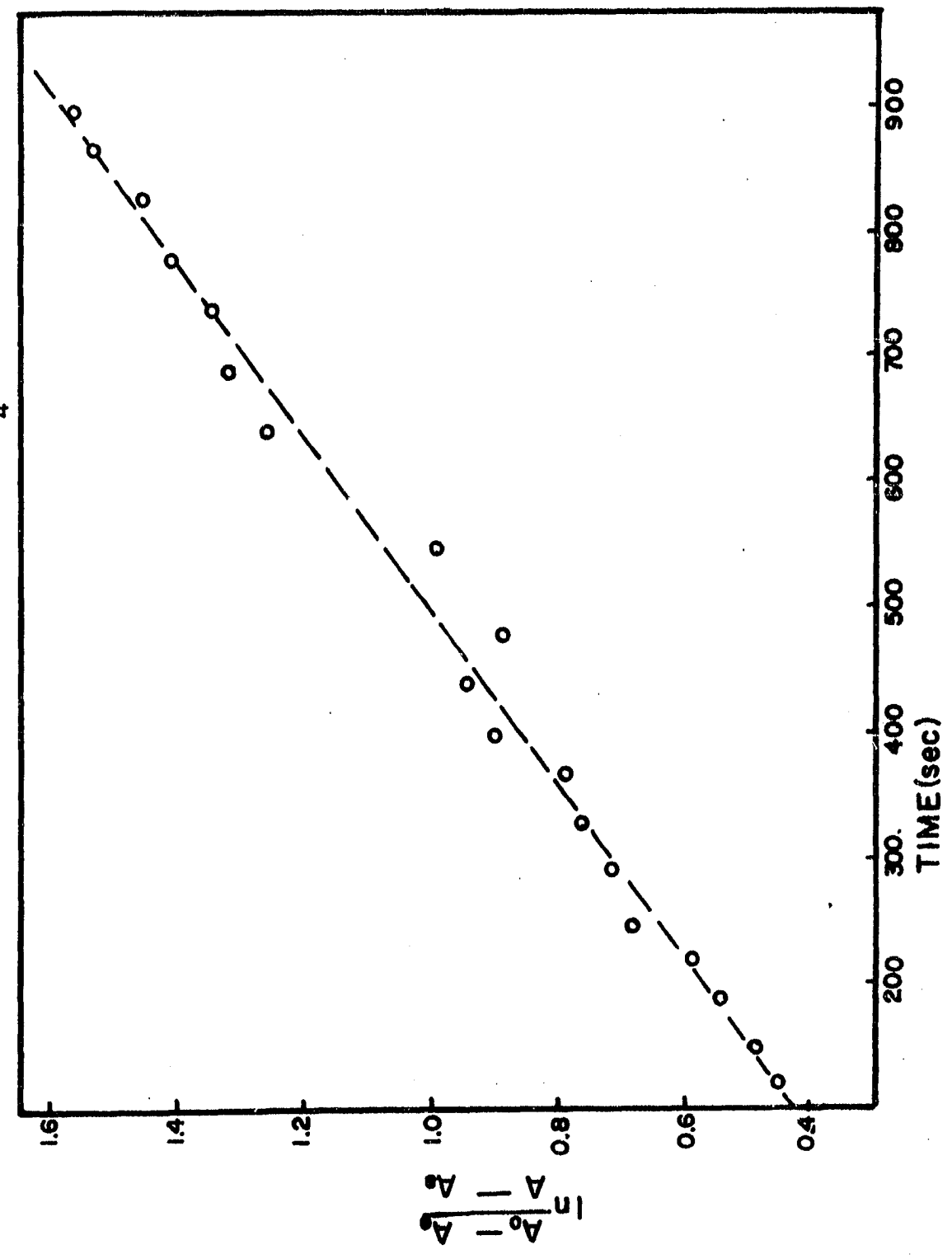

Figure A-13. Graph of $\ln(A_o - A_e)/(A - A_e)$ vs. time for the Isomerization of E-1-Chloro-1,2-dimethylsilacyclopentane by 5×10^{-3}M HMPT in CCl_4 at 313°K.

Table A-19. Isomerization of E-1-Chloro-1,2-dimethylsilacyclopentane[a] (15a) by 5×10^{-3}M HMPT in CCl_4 at 318°K.

Time(sec)	Relative Area[b]		Time(sec)	Relative Area[b]	
	15a	15b		15a	15b
150	37	138	550	64	107
190	40	135	610	69	107
230	42	130	650	71	104
270	49	123	700	74	104
310	48	124	740	76	104
350	54	124	770	73	101
410	56	115	800	76	100
450	56	110	830	77	96
500	60	111			

[a] 0.9M in CCl_4

[b] From NMR

Figure A-14. Graph of $\ln(A_o-A_e)/(A-A_e)$ vs. time for the Isomerization of E-1-Chloro-1,2-dimethylsilacyclopentane by 5×10^{-3} M HMPT in CCl_4 at 318°K.

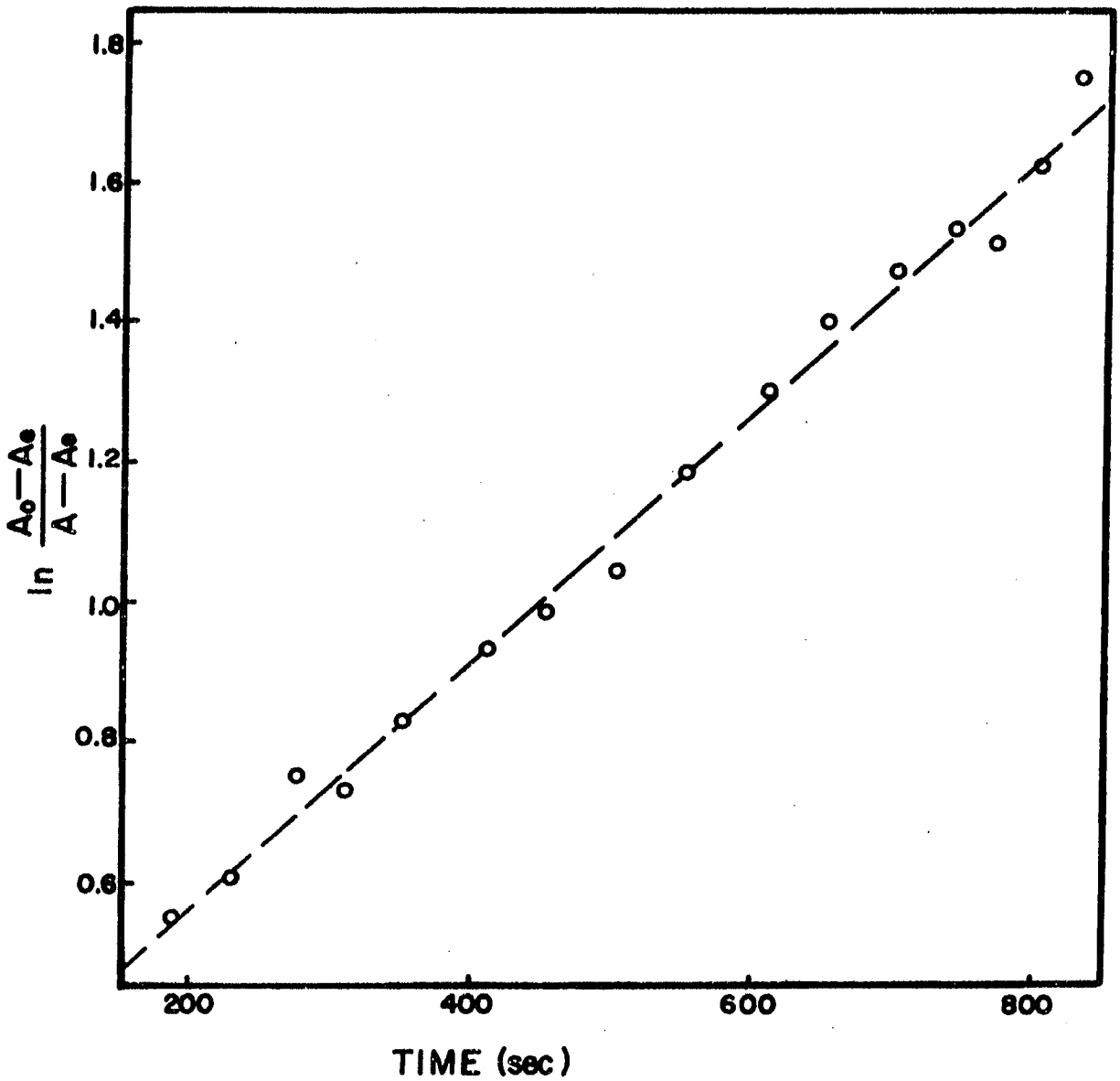

Table A-20. Isomerization of E-1-Chloro-1,2-dimethylsilacyclopentane[a] (15a) by 5×10^{-3}M HMPT in CCl_4 at 323°K.

Run 1			Run 2		
Time(sec)	Relative Area[b]		Time(sec)	Relative Area[b]	
	15a	15b		15a	15b
105	31	158	190	50	145
140	36	149	230	56	134
200	45	145	270	57	134
250	54	139	300	59	137
280	58	140	340	68	131
320	57	128	410	70	126
360	59	130	450	76	123
400	60	124	490	78	119
440	65	112	530	84	121
470	68	122	560	82	123
520	75	117	630	85	115
560	78	121	690	89	108
600	83	123			
640	80	108			

[a] 0.9M in CCl_4

[b] From NMR

Figure A-15. Graph of $\ln(A_o-A_e)/(A-A_e)$ vs. time for the Isomerization of E-1-Chloro-1,2-dimethylsilacyclopentane by 5×10^{-3} M HMPT in CCl_4 at 323°K (Run 2).

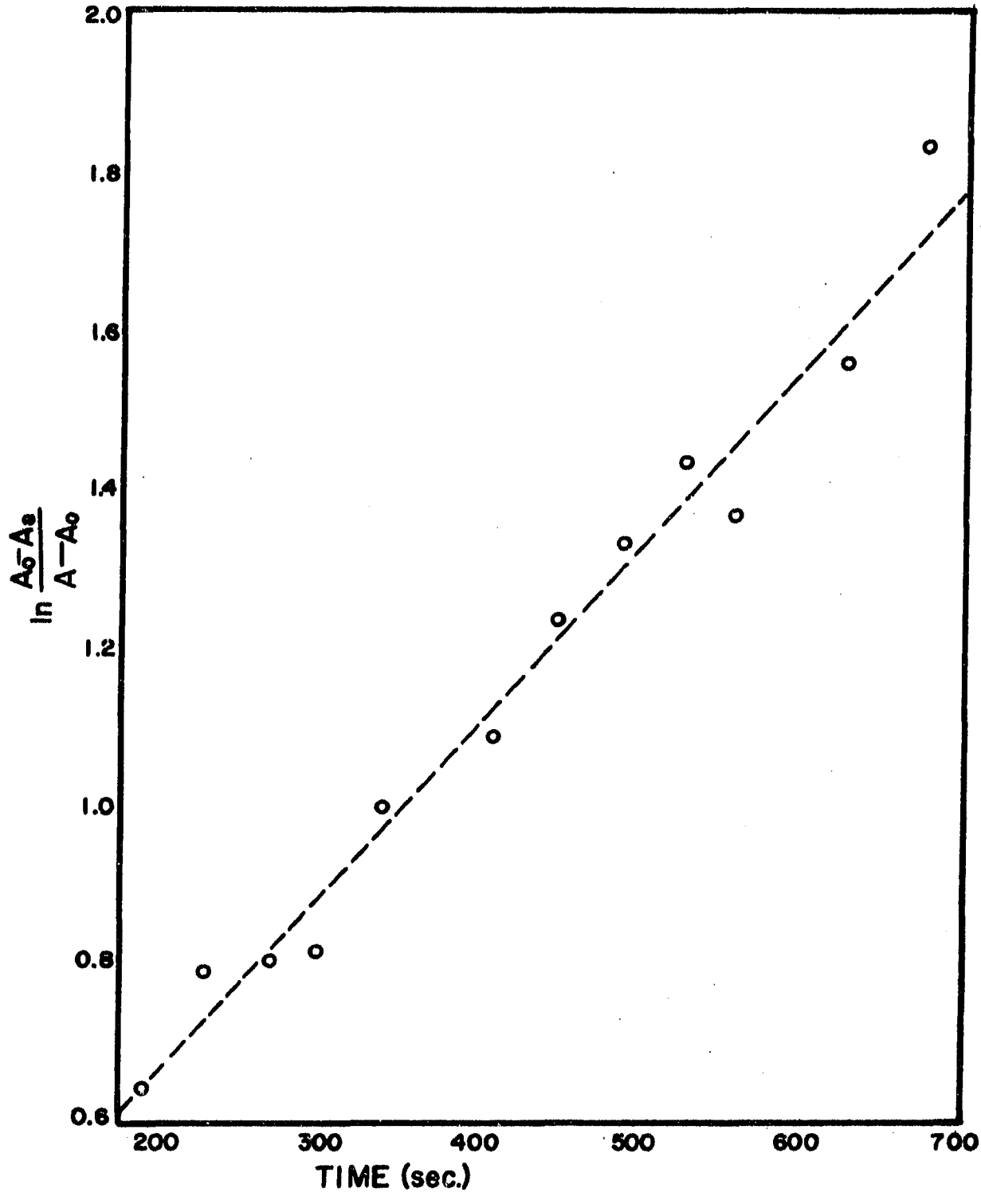

Table A-21. Isomerization of E-1-Chloro-1,2-dimethylsilacyclopentane[a] (15) By 5 x 10^{-3}M HMPT in CCl_4 at 328°K.

Run 1			Run 2		
Time(sec)	Relative Area[b]		Time(sec)	Relative Area[b]	
	15a	15b		15a	15b
120	38	143	90	40	146
150	40	149	130	43	149
180	43	137	170	51	154
220	49	129	230	57	135
250	53	130	270	60	132
290	56	126	311	66	128
330	59	121	350	68	125
360	63	127	400	73	128
400	67	115	440	77	117
430	67	116	480	76	111
470	66	109	540	81	109
510	73	107	570	85	112
550	74	104	630	92	114
580	79	102	660	89	106
620	80	102			
670	82	100			

[a] 0.9M in CCl_4

[b] From NMR

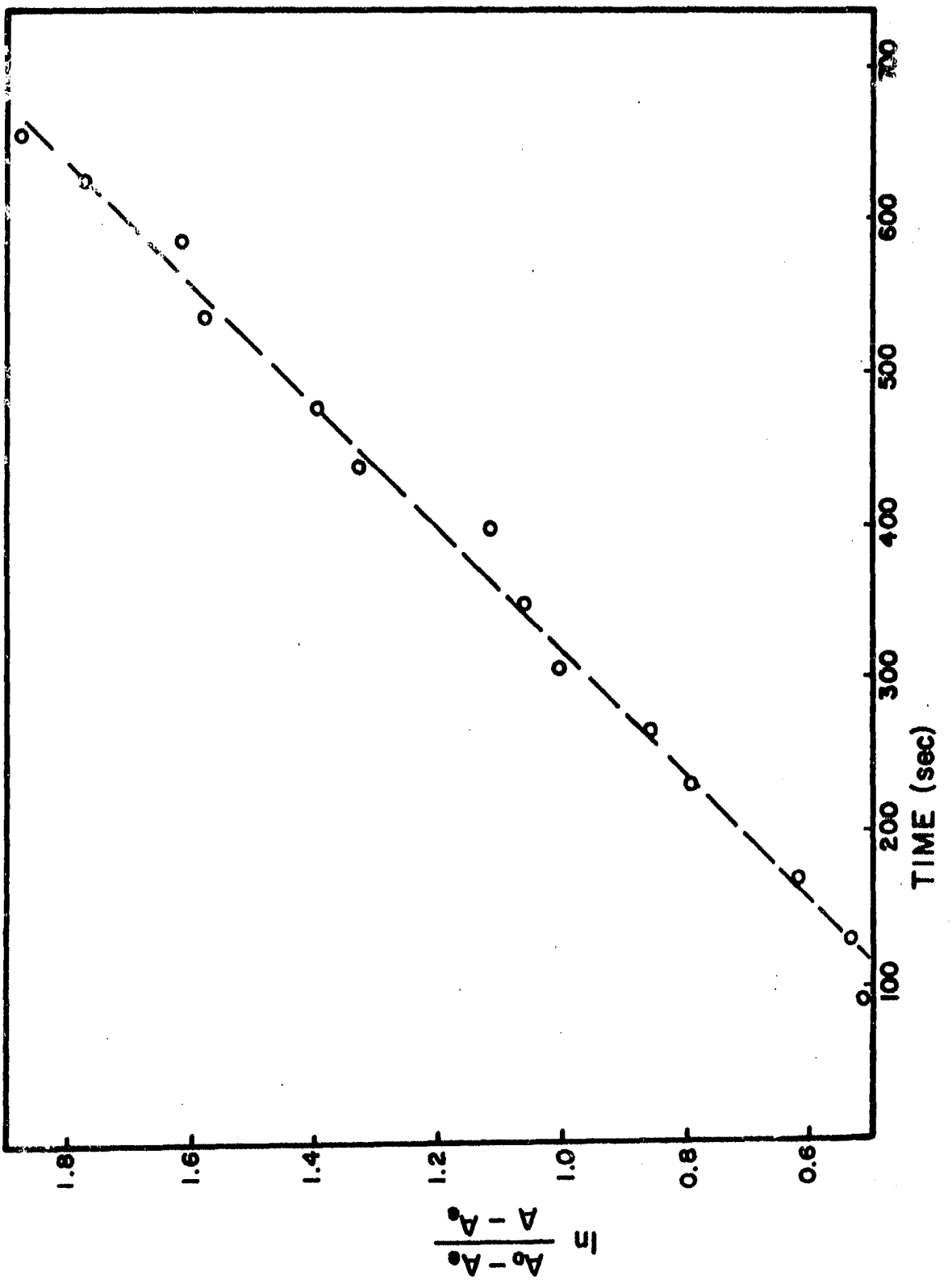

Figure A-16. Graph of $\ln(A_o - A_e)/(A - A_e)$ vs time for the Isomerization of E-1-Chloro-1,2-dimethylsilacyclopentane by 5×10^{-3}M HMPT at 328°K.

Table A-22. Rate Constants for the Isomerization of 15a by HMPT as derived from the data in Tables A-14 to A-21.

Table	Temperature	$k_{obs} \times 10^4$, sec^{-1}	$k_f^* \times 10^4$, sec^{-1}	r
A-14	277°K	4.3 ± 0.3	2.3 ± 0.2	0.987
A-15	287	6.1 ± 0.3	3.3 ± 0.2	0.992
A-16	296	9.4 ± 0.4	5.1 ± 0.2	0.996
A-17	308	14.2 ± 0.9	7.6 ± 0.5	0.991
A-18	313	14.4 ± 0.7	7.7 ± 0.4	0.994
A-19	318	17.8 ± 0.7	9.6 ± 0.4	0.996
A-20(Run 1)	323	21 ± 1	11.3 ± 0.5	0.992
A-20(Run 2)	323	22 ± 1	11.8 ± 0.5	0.988
A-21(Run 1)	328	25 ± 1	13.3 ± 0.5	0.994
A-21(Run 2)	328	25 ± 1	13.2 ± 0.5	0.997

Table A-22a. Activation Parameters for the Isomerization of 15a by HMPT as derived from the Graph of ln k_f vs 1/T. Figure A-17.

Ea (kcal/mole)	$\Delta H^{\ddagger}$ (kcal/mole)	$\Delta S^{\ddagger}$(cal/mole°K)	r
6.15 ± 0.07	5.54 ± 0.07	-55.0 ± 0.5	0.997

*k_{eq} = 1.1645

Figure A-17. Graph of ln k_f vs 1/T for the Isomerization of E-1-Chloro-1,2-dimethylsilacyclopentane by HMPT.

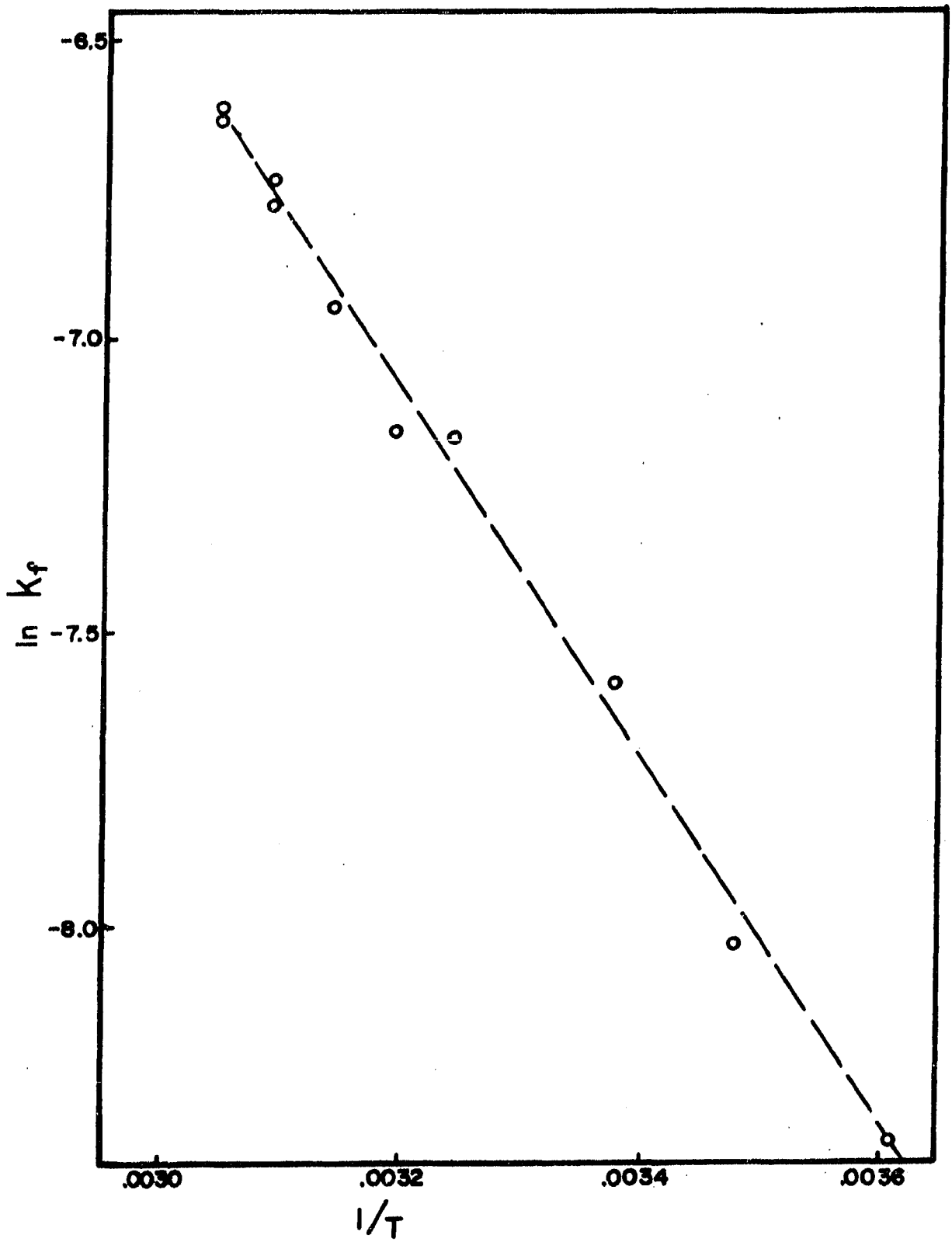

Table A-23. Isomerization of E-1-Chloro-1,2-dimethylsilacyclopentane[a] (15a) by 2.6×10^{-5} M n-Bu_4NBr in CCl_4 at 45°C.

Run 1			Run 2		
Time(min)	Relative Area[b]		Time(min)	Relative Area[b]	
	15a	15b		15a	15b
0.17	20	146	1.75	29	126
0.83	24	132	2.08	40	148
1.75	28	123	2.50	44	146
2.67	42	153	3.00	50	140
3.17	44	155	3.50	55	145
3.50	48	149	3.83	54	142
4.00	47	140	4.25	59	139
4.83	57	134	4.67	63	135
5.25	58	134	5.08	63	134
5.75	61	132	5.58	66	123
6.42	63	136	6.00	71	126
7.00	66	133	6.42	74	126
7.42	68	127	6.75	77	127
8.00	69	122	8.00	80	125
8.50	70	123	8.50	78	119
8.92	72	122	9.00	80	121
9.75	76	118	9.83	83	116
10.17	75	120			

Table A-23a. Rate Constants for the Isomerization of 15a by nBu_4NBr as derived from the Data in Table A-23.

Run	$k_{obs} \times 10^3$ (sec^{-1})	$k_f \times 10^3$ (sec^{-1})	r
1	1.76 ± 0.08	0.95 ± 0.04	0.995
2	2.2 ± 0.2	1.1 ± 0.1	0.989

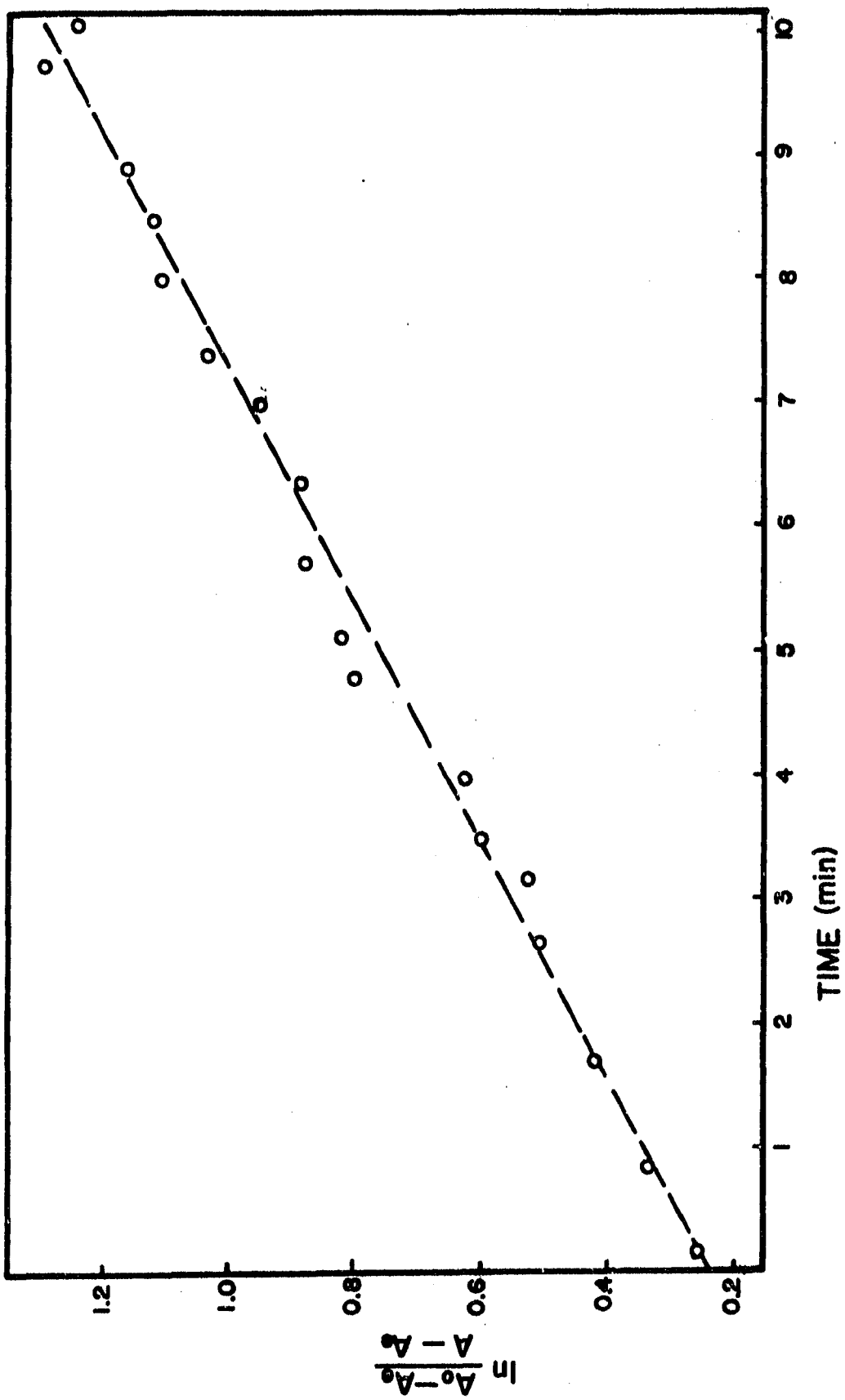

Figure A-18. Graph of $\ln(A_o-A_e)/(A-A_e)$ vs time for the Isomerization of E-1-Chloro-1,2-dimethylsilacyclopentane by 2.6×10^{-5} M n-Bu_4NBr at 45°C (Run 1).

VITA

Joanne Marie Moreau Wolcott was born on February 11, 1948 in Baton Rouge, La., where she was educated in the parochial school system. In May, 1966, she graduated from St. Anthony High School.

She entered Louisiana State University in June, 1966, and was awarded the Dow Chemistry Scholarship in her senior year. She received the degree of Bachelor of Science in Chemistry in May, 1970.

The following June, she entered the Graduate School of Louisiana State University, where she is now a candidate for the degree of Doctor of Philosophy in Chemistry.

On May 2, 1970, she married Duane K. Wolcott of Innis, La.

She is a member of the American Chemical Society and Iota Sigma Pi. She has worked as a Laboratory Technician at Shell Chemical Co. for the summers of 1968 and 1969. She was an NSF Research Assistant at LSU during Fall of 1972, and was a Research and Teaching Assistant from 1970-72 and 1973-75.

EXAMINATION AND THESIS REPORT

Candidate: Joanne Moreau Wolcott

Major Field: Chemistry

Title of Thesis: Studies with Silicon Heterocycles

Approved:

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

Date of Examination:

July 18, 1975